Chemical Engineering Integrated Master

Statistical Study for Yarn and Process Approval

Master Thesis

by

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Continental - Indústria Têxtil do Ave, S.A.

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Abstract

The present project results from the ongoing collaboration between Faculdade de Engenharia da Universidade do Porto and Continental- Indústria Têxtil do Ave. Indústria Têxtil do Ave is a part of the Continental Group and is one of the two units responsible for producing textile reinforcements for tire applications.

There are several testing methods that are applied during the manufacturing process in order to verify the properties of the fiber and the final product. Until now, in the Product Industrialization Laboratory, a random number of samples (spools) are selected to this end with no particular order or method.

The objective of this dissertation is to determine how many samples (spools) need to be tested in order to ensure, with a certain confidence level and associated precision, the properties of the products. The methodology developed is applied to the existing products. The number of samples required to test regarding most test methods was determined for nylon with 940 decitex and polyester with 1440 decitex. Furthermore it was possible to determine which of the test methods currently comply with the required precision.

It was implemented a method for sample sizing that requires 30 spools of the product whose characteristics are necessary to assess. It can be concluded that test methods applied comply with the requirements. Furthermore, it was possible to conclude that different types of fibers influence the number of spools required to test.

Key words: Statistics; Distribution Analysis; Textile Reinforcements; Tire

Resumo

A presente dissertação resulta da colaboração entre a Faculdade de Engenharia da Universidade do Porto e a Continental- Indústria Têxtil do Ave. A Indústria Têxtil do Ave é uma de duas unidades responsáveis pela produção de reforços têxteis para aplicação em pneus.

Existem vários métodos de ensaio que são aplicados durante o processo de fabrico, de modo a verificar as propriedades da fibra e do produto final. Até agora, no Laboratório de Industrialização de Produto, um número aleatório de amostras são selecionadas para este fim, sem ordem ou método estabelecido.

O principal objetivo da presente dissertação é determinar quantas amostras (bobinas) precisam ser testadas, a fim de garantir, com um nível de confiança e precisão associada, as propriedades dos produtos. A metodologia desenvolvida pode ser aplicada aos produtos existentes. O número de amostras necessárias em relação a maioria dos métodos de ensaio foi determinado 2 produtos nylon com 940 decitex e poliéster com 1440 decitex. Além disso, foi possível determinar quais dos métodos de ensaio estão em conformidade com a precisão necessária.

Foi implementado um método para a determinação do número de amostras que requer 30 bobinas de produto cujas características são necessárias avaliar. Pode concluir-se que grande parte dos métodos de teste aplicados está em conformidade com as exigências. Além disso, foi possível concluir que diferentes tipos de fibras influenciam o número de amostras necessárias.

Palavras chave: Estatística; Análise de Distribuição; Reforços Têxteis; Pneu

Declaration

I declare, under honor commitment, that the present work is original and that every non-original contribution was properly referred, by identifying its source.

Porto, 31st July 2014

(Gisela José de Castro Lima)

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Notation and Glossary

dtex	Decitex (g×10 000 m^{-1})
tpm	Turns per Meter
μ	Population Standard Mean
σ^2	Population Variance
n	Sample Size
$\overline{X}$	Sample Mean
α	Significance Level
z	Standard Score
E	Margin of Error
S^2	Sample Variance
S	Sample Standard Deviation
H_0	Null Hypothesis

List of Acronyms

C-ITA	Continental- Indústria Têxtil do Ave
LTU	Laboratory Twisting Unit
LDU	Laboratory Dipping Unit
ASTM	American Society of Test Methodology
PET	Polyester
RFL	Resorcinol-Formaldehyde-latex
FASE	Force at Specific Elongation
Gage R&R	Gage Reproducibility and Repeatability Study
ISO	International Standards Organization

1 Introduction

1.1 Project presentation and framework

Nowadays it is known that up to 17 % of all car accidents are related to malfunctions; in fact, two thirds of these are due to tires defects.[1] To minimize the number of malfunctions, every component of a tire is manufactured so that the final product is as perfect and flawless as possible and also endures the conditions to which it is exposed to.

All tires include three types of reinforcements: rubber compounds, steel and textile cords. The application of textile reinforcements in tires is necessary to avoid rubber deformations when excessive forces are applied. These forces result from air pressure of the tire, when accelerating, breaking and cornering of the car. [2] Textile reinforcements are mainly applied on the carcass and cap-ply. In a typical radial tire there are up to 25 different structural parts and as many as 12 different rubber compounds.[3] The typical radial tire cross section is shown in Figure 1.

Description:

1. Tread

2. Jointless cap plies

3. Steel-cord belt plies

4. Textile cord ply

5. Inner liner

6. Side wall

7. Bead reinforcement

8. Bead apex

9. Bead core

Figure 1- Cross-sectional view of a typical tire. Adapted from [4]

The tread is the thickest component of the tire and is in direct contact with the road, providing grip on all road surfaces, wear-resistance and direction stability. The base of the tread is related to rolling resistance. Due to its high thickness, the tread aggravates cyclic energy losses, increasing temperature and therefore causing intensification of fuel consumption. Jointless cap plies, which consist mostly in nylon embedded in rubber, enhance high speed suitability and act as a barrier restricting migration of chemicals from the tread to the belt. Steel-cord belt plies provide rigidity and a stable foundation to the tread region which enhances performance, vehicle stability, handling performance simultaneously protecting ply cords. As stated before, textile cord plies usually rubberized rayon or polyester, control internal pressure and help to preserve the tire's shape. The inner liner, whose main function is to retain compressed air inside, is predominantly bromobutyl-isoprene rubber.[4, 5]

The present work took place at Continental- Indústria Têxtil do Ave S.A. (C-ITA). In recent years, C-ITA's product industrialization laboratory became a reference laboratory among the Continental corporation and currently optimizes existing products, creates new textile reinforcements and solves pre-existent dip and other adhesion related issues. This project emerges from the necessity to study the variation of the test methods currently applied and existing products in order to determine how many samples need to be tested to ensure the properties of a specimen with a certain level of confidence and margin of error associated.

In this context, the validation of a set of test methods shows if the method fits its intended purpose. This includes an assessment and balancing of technological possibilities, risks and costs. In the validation process the ultimate aim is to secure that the test methods are adequate regarding repeatability, reproducibility and also representativeness.

1.2 About Continental

The automotive industry is one of the most competitive and secretive industries around. Continental is one of the top 5 automotive tire suppliers worldwide, the second in Europe, with 195 production sites, located in 35 different countries.[6] At the end of the present year, Continental estimates to employ about 185 000 people worldwide.[7] Currently, Continental has two producers for textile reinforcements, one in the USA and the other in Portugal. ITA was founded in 1950 in Lousado, Portugal, becoming an integrated part of the Continental group since 1987.[8]

At C-ITA, diverse types of fibers arrive from around the world. Then, fibers are twisted into different cords and dipped as individual cords or fabric to improve adhesion between cords and the rubber compound. At laboratory scale, the twisting and dipping processes are simulated in a Lab Twisting Unit (Figure 2) and Lab Dipping Unit (Figure 3). This allows the development of new textile reinforcements, optimization and the attempt to solve existing problems without interrupting normal production, in a less time consuming and costly method.

Figure 2- Laboratory Dipping Unit (LDU)

Figure 3- Laboratory Twisting Unit (LTU)

1.3 Project Objectives

At the end of the present project it will be possible to understand which methods currently applied at C-ITA comply with the required precision. Furthermore, a better understanding of variation of different fibers and its influence on the number of samples that require testing can be achieved, so it will be possible to know the exact number of spools that require testing in two specific products: nylon 940 dtex and polyester 1440 dtex.

1.4 Work Contributions

The present work is the first approach to study variation between spools at C-ITA. It will be possible to understand the existing variation inherent to each test method and also evaluate the influence of the raw material and supplier on the existing variation. These types of studies are important to validate test methods and also characterize processes and products.

These sets of experiences were developed by the author. Procedures and the methodology followed were developed by C-ITA according to American Society of Test Methodology (ASTM) procedures. When necessary, adjustments were made in order to minimize repeatability problems.

1.5 Thesis Organization

The present master thesis is structured in 6 main chapters, briefly described in the following paragraphs.

Chapter 1- **Introduction** frames all the work done providing a general overview about this project and its main objectives.

Chapter 2- **State of the art** – describes textile reinforcements, giving information about the technology, the manufacturing process and variables that apply to this type of reinforcements. Additionally, a statistical approach is introduced including some facts about size sampling, standard deviation, among other concepts.

Chapter 3- **Materials and Methods –** provides all the experimental work procedures including materials, test methods and testing instruments.

Chapter 4- **Results and discussion** – presents all the outcomes of the tests performed.

Chapter 5- **Conclusions** – summarizes the main conclusions of the developed work.

Chapter 6- **Project assessment** – evaluates the work done and the achievement of objectives and defines some of the future work.

2 State of the Art

2.1 Reinforcement Materials

Steel cords satisfy the requisites for a stiff, high modulus and strength material at an acceptable cost, presenting also good resistance and adhesion to rubber while textile reinforcements present the capacity to elongate simultaneously providing stability and rigidity among other advantages previously mentioned. Cotton, polyester (PET), nylon, rayon and aramid are the raw materials used to manufacture textile reinforcements.[9]

Since the introduction of synthetic fibers, cotton has increasingly been replaced. Cotton is a natural cellulose fiber that absorbs humidity from air (up to 8 % weight increase). It has a good resistance to heat up to 150 ºC but with prolonged exposure loses significant strength. The main advantages of cotton are its price, moderate strength and capacity of adhesion, but these are easily surpassed by disadvantages like quality variations and high softness.[9]

Rayon is made from regenerated cotton fibers usually from wood pulp or cotton. Although it is more expensive and is sensitive to moisture, rayon has more strength than cotton, presenting good resistance to heat, high modulus and good resistance to fatigue. There have been some special types of rayon developed for ultra-high performance tires that show high dry/wet strength, good dimensional stability and other appealing physical properties.[9]

Polyester (PET) is another widely used synthetic fiber that has as main disadvantage poor adhesion to the rubber compound, requiring some pre-treatment known as activation, because it is chemically inert and has low shrinkage. Although polyester is not as resistant to heat as rayon and nylon, it presents advantages such as high stiffness, good dimension stability at high temperatures and good resistance to water.[9]

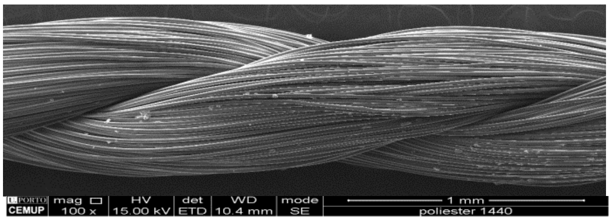

Figure 4- Scanning Electron Microscopy image of PET 1440 dtex

The substitution in polyamides of aliphatic groups with aromatic groups results in aramids. These fibers show the highest resistance to temperatures up to 250ºC but display loss of strength by ultraviolet light exposure. The main advantages of aramids are high strength and stiffness and good dimension stability although aramids present disadvantages like weak adhesion and low fatigue resistance.[9]

Nylon (Ny) is the generic name for the linear aliphatic polyamides. In tires, nylon is mostly applied in the cap-ply. Nylon displays high strength and resistance to heat and has good capability of forming bonds with rubber compounds. The elongation at specific force for diverse types of fibers are in Figure 5.[9]

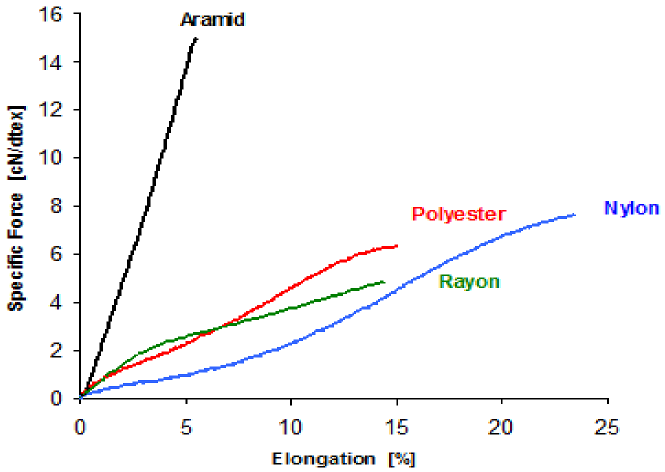

Figure 5- Comparison of elongation at specific force for diverse types of fibers. Adapted from [10]

Nowadays, especially for high performance tires, the development of hybrid cords, which are two or more combinations of different types of yarns, is interesting due to the combination of properties resultant, causing the minimization of the disadvantages of each yarn in its conventional form. Also for ultra-high performance tires, the creation of thin (low decitex) hybrid cords allows the reduction of the total weight of the textile reinforcement thus decreasing the total weight of the car.[11]

2.2 Manufacturing Textile Reinforcements

The industrial process of textile reinforcements is divided by four stages and results in two final products, dipped cords or dipped fabric. The first step of the manufacturing process is spinning, in this particular case completed outside C-ITA by the yarn suppliers. There are different types of spinning such as dry spinning, wet spinning, gel spinning and melt spinning that are applied to each fiber depending on physical and chemical properties. [12]

The following step is the twisting process. The yarn without treatment, designated by greige yarn at this stage, is twisted in order to improve the elongation and fatigue resistance of the textile. The cord construction begins with twisting the yarns individually in the *z* direction followed by the twisting of multiple yarns in the *s* direction thus constructing a cord. The third stage is the weaving process were greige cords are placed next to each other and distributed equally throughout the fabric.[10]

The last step in the textile reinforcements production process is the dipping. In order to reach required adhesion and desired mechanical properties, the cords or fabric are dipped in a water, resorcinol, formaldehyde and latex (RFL) emulsion and then stretched through drying in the ovens at the optimum conditions consequently enhancing the properties of the fibers. The dipping solutions also vary according to each fiber utilized. Parameters such as ratio formaldehyde/resin, latex/resin, cure time and temperatures can be modified. In some cases, for example most PET and some aramids fibers, the cords are previously dipped in a solution consisting mostly on isocyanates and poliepoxy named pre-dip. The schematic design of the textile reinforcement manufacturing process is shown is Figure 6.[10]

Figure 6- Schematic representation of textile reinforcements production process

2.3 Characterization

The final characteristics of tires are deeply related to the reinforcements properties. The tire performance and related tire cord properties are presented in Table 1.

Table 1-Tire performance and related tire cord properties. Adapted From [13]

Tire Performance	Related Properties of Tire Cords
Bursting Strength	Tensile Strength
Tire Endurance	Adhesion with Rubber
Power Loss	Viscoelastic Properties
Tread Wear	Modulus
Tire Size and Shape	Modulus
Flat Spotting	Thermal Shrinkage
High Speed Resistance	Heat Resistance

In order to meet criteria, there are properties analyzed in each cord such as twist level, yarn modulus, force at specific elongation (FASE), breaking force, thermal shrinkage, thermal shrinkage-force and adhesion to the rubber.

Linear Density

Linear density of a yarn can be regulated by changing the number of filaments. This characteristic can influence the properties of the cords. For example, in nylon cords breaking strength and modulus increase for higher linear densities. Linear densities are usually expressed in tex or most commonly decitex (dtex) which represents the mass of the fiber expressed in grams per 10 000 meters. For dipped cords, the mass of the cord is expressed in grams per one hundred meters and referred to as weight per length.[14]

Load-Elongation

One of the most important parameters in fibers and constructed cords result from load-elongation curves (see Figure 5). The following properties can be obtained:[15]

- Load- Force applied to a yarn or cord, expressed in N;
- Young Modulus- Slope of the load-elongation curve where load and elongation are proportional, expressed in N/%;
- Breaking Strength- Maximum force required to break a yarn or a cord, expressed in N;
- Tenacity- Corresponds to specific strength which means breaking strength per linear density, expressed in N/tex;
- Elongation- Represents the amount of elongated yarn or cord when subjected to a force, expressed in %;
- Force at Specific Elongation (FASE)- Force required to obtain a specific elongation, expressed in N;
- Elongation at Break- Total elongation of the cord until breaking, expressed in %.

Thermal Shrinkage and Shrinkage-Force

Thermal Shrinkage is the amount of shrinkage of the cord while subjected to heat for an established time frame. Shrinkage forces result from thermal shrinkage testing. When testing for thermal shrinkage, the most influential variable is the type of polymer selected since shrinkage is mostly dependent on the amorphous parts of the cord. By increasing the degree of stretching, results a significantly higher shrinkage of the fiber.[16, 17]

Twist Level

The industrial twisting process is complex and can result in different cords. The twist level in each cord influences mostly the elongation of the cords and both yarn and cord can have balanced or unbalanced twist. For both nylon and pet cords, the increase of twist factor causes breaking strength to decrease while breaking elongation increases. Shrinkage, adhesion and fatigue resistance also increase if the twist level is increased. When twist is applied to any textile yarn the breaking strength increases to a maximum value (optimum twist level) and then decreases regardless of the type of material. This is due to the fact that increasing twist also increases the angle between cord axis and filament axis. That explains why cords with higher twist show low breaking strength but high fatigue resistance.[18, 19] In Figure 7 an example is shown.

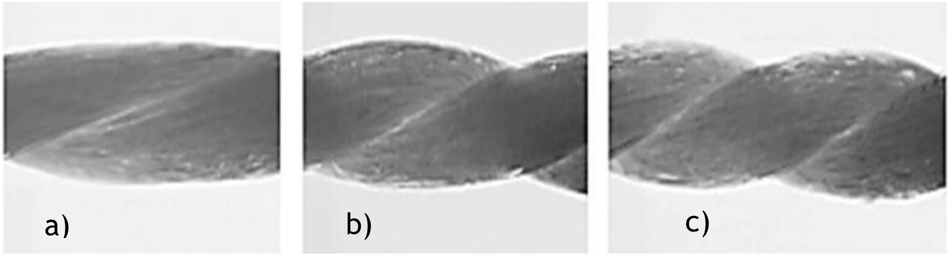

Figure 7- Polyester cords with different twist levels a) 200 tpm; b) 350 tpm; c) 470 tpm. Adapted from [18]

Ply Difference

Besides twist level, the length difference (usually expressed in mm) between plies in a multiple ply cord construction helps to ensure that the cords are correctly twisted. For a two ply construction cord, one meter of cord is taken, untwisted and each ply length is measured again. The difference in length in the first ply (l_1) and the second ply (l_2) constitutes ply difference (Δl). [10] A schematic example is shown in Figure 8.

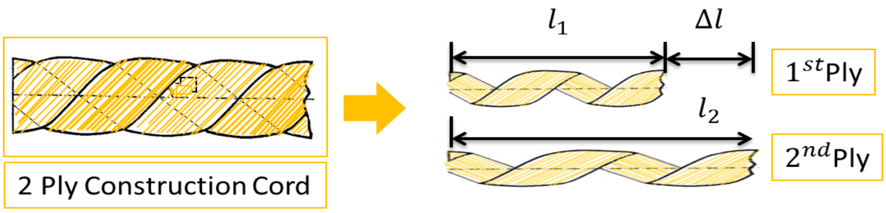

Figure 8- Example of ply difference on a two ply construction cord. Adapted from [10]

Peel Adhesion Test

Peel adhesion tests are usually applied in order to evaluate tire cords or tire cords fabrics and also evaluate the process of adhesive reaction on the cord. For high safety and high performance products such as tires, good adhesion between fibers and rubber is essential. Besides the type of fiber, the dipping solution is the variable that most influences adhesion. Those water based emulsions contain chemical agents that will bond the fiber to the rubber.[2, 20]

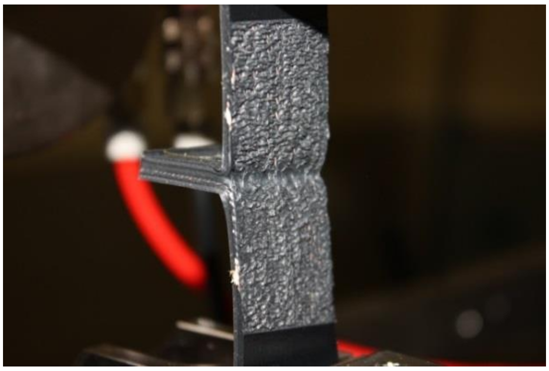

Figure 9- Peel Adhesion test sample

H Test

Besides the peel adhesion test, the H test is another method to evaluate adhesion between dipped cords and rubber compounds. The H test is applied to evaluate tire cords by pulling the cord in the direction of its axis from one of the two strips of rubber in which the cord is inserted. There are many variables that can influence the results of this test method such as fiber type, cord construction and thickness as well as rubber type and cure, among other aspects. Due to repeatability problems this test method is performed at least ten times.[21]

Dip Pick-up

The amount of dip that remains on the cord after the dipping process is called dip pick-up. The adhesion increases as function of dip pick up until it reaches a saturation point. The optimum amount of dip pick-up is around 7 wt %.[2] The amount of dip pick-up is determined by dissolving the textile sample using a suitable solvent and determining the remaining dip gravimetrically. Any remaining fibers or materials may contaminate the sample and greatly influence the results.[22]

2.4 Statistical Analysis

For the validation of test methods, there is the necessity to prove reliability. This includes verification of environment and storage conditions, human factors, calibration methods, equipment and procedures. Furthermore, accuracy and precision, repeatability, reproducibility and uncertainty studies are necessary. Standards ISO 17025 (General requirements for the competence of testing and calibrating laboratories), ISO 5725 (Precision of test methods-Determination of repeatability and reproducibility for a standard test methods by inter-laboratory tests) and ISO 21748 (Guidance for the use of repeatability, reproducibility and trueness estimates measurement uncertainty estimation) provide valuable guidance for improving the quality of the experimental results.[23-25]

To determine how many samples need to be tested to each state of the yarn/cord it is required to characterize the targeted population, the deviations associated to each test and to evaluate the methods applied. Therefore, the following step is sample sizing.

There are several approaches to sample sizing. Usually one conducts a pilot study and then uses the standard deviation resultant from within that study or estimates the standard deviation from previous studies using the same population of interest. As last resource, the range of the variable analyzed divided by 4 can be an estimate of the standard deviation.[26] In this work, sample sizing was based on the Central Limit Theorem. This theorem implies that for a random variable following any distribution with standard mean (μ) and variance (σ^2), the higher the sample size (n), the better the chance that the distribution of the sample mean ($\bar{X}$) will follow a normal distribution. For practical reasons it is considered that any sample size equal or superior to 30 will suffice regardless of the shape and size of the original population. In this master thesis, the assumption that a sample of 30 spools is enough for the distribution of means to follow a normal distribution was taken. Mathematically, for a 95 % confidence interval and margin of error (E) this implies the conclusions explicit in Equation 2.1.[27, 28]

$$z\alpha/_2 \times \frac{\sigma}{\sqrt{n}} = E \Leftrightarrow n = \left(\frac{z\alpha/_2}{E} \sigma \right)^2 \tag{2.1}$$

In most trials and studies the margin of error is defined as a percentage of the mean. The significance level (α) and standard score (z) are established according to the confidence level. Some values for standard score are expressed in Annex I. For most statistical tests it is necessary to ensure levels of confidence superior to 90 %, normally 95 % or 99 %.[27, 28]

The main advantages of a known distribution especially one like the normal distribution are the small number of parameters to adjust and the shape of the distribution that facilitates models and mathematical fitting. Besides, advanced statistical techniques usually assume normal distribution of data. One of the parameters that describe normal distributions is the sample or population mean (μ). Let $X_1, X_2, X_3, \dots, X_n$ be a sample of values extracted from the population. The sample mean ($\bar{X}$) is defined by the Equation 2.2.[27, 28]

$$\bar{X} = \sum_{i=1}^{n} \frac{X_i}{n} \tag{2.2}$$

It is also necessary to characterize the spread or variability of the data values. This is accomplished by the sample variance (S^2). The positive square root of the sample variance is called sample standard deviation (S). The sample standard deviation is obtained according to Equation 2.3. With these two parameters fully disclosed, the normal distribution is totally characterized.[27]

$$S = \sqrt{\sum_{i=1}^{n} \frac{X_i - \bar{X}}{n-1}} \tag{2.3}$$

There are several statistical tests suitable to draw conclusions from a data set. The first stage of correctly analyzing data is to qualify that set. From a statistical point of view there are two main types of data, categorical and numerical. Categorical data consists of counts or observations that can be classified into categories that may or may not be descriptive whereas numerical data is expressed by numbers. In its turn, numerical data can be considered discrete or continuous.[27, 28]

The following step is to identify the parameters of the data distribution. The methods that rely on the knowledge of the specific distributions of the population are entitled parametric tests. All the others are called non-parametric tests. In general, parametric tests are capable of better qualification with less deviations and errors than non-parametric tests. Nevertheless, non-parametric tests are capable of better results when dealing with outliers or non-detect errors. Any assumptions made up to this stage should then be subjected to tests of assumptions. If necessary, corrective actions should be performed in order to not compromise the study.[27]

There are several methods to determine if the population follows the normal distribution depending on the sample size and the type of data. One of the most powerful tests for normality is the *Shapiro-Wilk* test. In this master thesis, the Shapiro tests of normality were completed using the statistical software *R*®. The *Shapiro-Wilk* test is recommended for a limit of 2000 samples. The test results in two values, *W-value* and *p-value*. The *W-value* varies from 0 to 1, 0 when the sample data does not follow the normal distribution and 1 when the sample data are perfectly normal. So the closer the *W-value* is to 1, the closer the data fit the normal distribution. The *p-value* is the smallest level of significance that would lead to rejection of the null hypothesis (H_0) with the given data. In normality tests, the null hypothesis is that the observed distribution fits the normal distribution. This hypothesis is the opposite of the alternative hypothesis which implies that the observed distribution does not fit the normal distribution. For a 95 % confidence interval the null hypothesis should be rejected if *p-value* is inferior to 0.05. It is customary to call the test statistic (and the data) significant when the H_0 is rejected. Many times *p-values* and *W-values* can be misleading. To avoid errors plotting the data is useful since it can lead to identification of patterns and outliers. Histograms, box plots, steam and leaf plots and quantile comparison plots (Q-Q plots) are some of the graphic tools applied.[27, 29]

As mentioned earlier, repeatability and reproducibility studies are necessary. Repeatability is a measurement of variation using a single operator and single instrument on the same sample, over a short amount of time with the most number of variables possible held constant.

Reproducibility attempts to measure variations with multiple operators and/or multiple instruments and/or multiple locations with the same sample lot.[30]

Gage Repeatability and Reproducibility studies (*Gage R&R*) are capable of determining how much of the overall observed variation is due to measurement system variation. These studies include variance, standard deviation, the percentage of contribution of each factor and the amount of study variation and most of the time includes statistical analysis studies like one way or multi-way analysis of variance (*ANOVA*).[31]

Mathematically, *Gage R&R* studies are based on statistical properties of data qualification such as bias and variance results. The total variation of the process is the sum of the variation introduced by reproducibility and repeatability issues and the variation naturally existent in products.[31]

3 Materials and Methods

The variations within the same spool were assumed negligible and all the spools were taken from the same lot to avoid variations between the samples. Repeatability issues were avoided by using the same operator, the same working conditions, within the minimum time frame possible. To minimize variations all the cords were divided into two spools and then twisted with the corresponding spool, resulting in 30 greige cords and after the dipping process, 30 dipped cords. As said before, all the cords were twisted in the LTU and then dipped in the LDU.

The requirements and guidelines for these set of test methods are applicable for all manufacturing units and divisions of Continental-AG, including the research and development groups, and also for suppliers.[22] Of all the tests currently approved at C-ITA, some tests such as dip pick-up and stiffness were not performed because of the non-existing relations between the adjustments in production and laboratory scale. Besides, these tests demonstrate great variances and deficient repeatability and reproducibility results. All testing procedures were performed according to the method established with the exception of thickness and linear densities where the number of repetitions was increased from 3 to 5.

The laboratory temperature and humidity is currently conditioned according to ASTM D1776 and ISO 139. The main goal of conditioning is to avoid high variations in moisture and temperature since it can affect the properties of the fibers. The conditioning environment in the laboratory is designed to obtain reproducible results on textile and textile products. In order to make comparisons between different textile samples and laboratories it is necessary to standardize humidity and temperature.[22,32] At C-ITA, the minimum conditioning time established for all fibers and cords is 24 hours. For one hole month, it was installed a temperature and humidity measuring device. The result of the measurements is exposed in Table 2.

Table 2- Measured and established temperature and humidity at the laboratory

	Established Values		Measured Values		
	Minimum	Maximum	Minimum	Maximum	$\bar{x}$[1]
Temperature / °C	21	25	21.9	27.0	22.9
Humidity / %	50	60	41.6	62.2	53.7

1 This average refers to 2700 measurements

3.1 Materials

In this master thesis the trials were performed using nylon with 940 dtex from supplier A and afterwards polyester with 1440 dtex from supplier B. Different fibers were studied to understand if different suppliers and fibers properties would influence the results obtained.

Nylon 940

At C-ITA, nylon 940 is the most commonly used and is applied in the cap-ply as a two ply cord. On nylon fibers, load at 2 % and 4 % elongation and thermal shrinkage are important characteristics to analyze due to the fibers proprieties. However the evaluation of twist level and peel adhesion force provide some of the proprieties that are evaluated for all fibers used for tire applications.

PET 1440

As said before, polyester is a very well-known reinforcement material usually applied in the carcass. This type of polyester requires pre-treatment with activation. Most of the proprieties analyzed for nylon cords are also analyzed for PET; nevertheless for this case thermal shrinkage is not as relevant because PET cords are not as amorphous. Also for load-elongation curves, the most important parameters for this material are breaking strength and load at 45 N.

3.2 Methods

The tests were performed on the greige yarn, greige cord and then dipped cord after relaxation. The dipped cord was placed out of the spool for at least 24 hours in order to relax and equilibrate within the environment. These conditions simulate the existing settings which textile fabric is exposed allowing comparisons between single cords and fabric to be established. The types of tests performed to the sample at each stage are in Table 3.

Table 3-Tests performed to nylon and polyester cords

	State of the yarn/cord		
Test	**Greige yarn**	**Greige cords**	**Dipped cord**
Decitex	✓	✓	×
Weight per length	×	×	✓
Load-Elongation	✓	✓	✓
Thermal Shrinkage	✓	×	✓
Shrinkage-force	✓	×	✓
Thickness	✓	✓	✓
Twist of the cord	×	✓	✓
Twist of the yarn	✓	✓	✓
Ply difference	×	✓	×
Peel Adhesion test	×	×	✓

Thickness

This test was only validated for dipped cords. Regardless of this fact, at C-ITA this test method is also applied to yarns and greige cords. This measurement requires a specific device consisting of an anvil diameter of about 10 mm and an anvil measuring pressure with minimum pressure of about 25 kPa; a dial gauge stand was utilized (Figure 10).

Figure 10- Thickness measuring device

The test consists on placing four cords or yarn pieces straight and parallel to each other on the anvil of the thickness gauge and measure thickness. At least three samples must be measured for each test and each sample consists of four yarns or cords that must be measured only once. Due to pre-existing thickness measuring issues that result from the lack of precision of the existing equipment two supplementary trials were performed.[22]

Linear Weight - Decitex and Weight per Length

This procedure is applicable for the determination of the weight of yarns, twisted and dipped cords. For yarns and twisted greige cords, a sample of 10 or 100 meters should be obtained using the device represented in Figure 11 Figure 11. For dipped cords the sample taken should be 1 meter long. Any damaged or unfit sample should not be used for testing. Afterward, the sample is dried in for one hour at 105 ºC in a Drying Chamber with ventilation. The final step is to weigh each sample in a precise balance with an error of 0.01 g.[22]

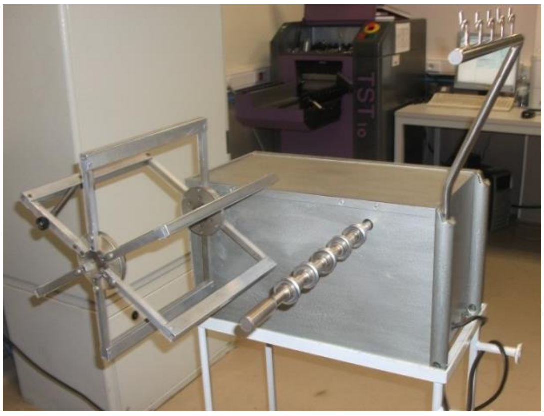

Figure 11- Decitex measuring device

Load-Elongation

To perform this type of test, the specimen must be conditioned according to ASTM D1776. The clamping length depends on the fiber of the sample.[22, 32,33]

Tensile tests were completed using a Zwick Roell tester, with cross head speed of 300 mm/min and gauge length of 254 mm according to ASTM D885. An average of 5 test runs were reported for each sample, either greige yarn, greige cords and dipped cords. [22, 32, 33]

Thermal Shrinkage and Shrinkage-Force

During these types of tests, temperature should not vary more than 2 ºC. The samples are placed on the measuring device and subjected to pre-tension according to the linear density.[22, 34]

Then, the samples are exposed to elevated temperatures for a specific amount of time. After that, the samples cool down while exposed to normal conditioning environment for 2 minutes. These properties were tested 5 times for each sample. Thermal shrinkage and shrinkage-force of the yarn and dipped cord were measured using a Lenzing Intruments Shrinkage Tester (Figure 12).[22, 34]

Figure 12- Thermal Shrinkage and Shrinkage-Force Tester

Thermal shrinkage is the difference in length before and after the sample is exposed to heat and tension during a period of time. The initial length of the sample, L_0, is then compared to the length after exposed to heat (L_1). Shrinkage is obtained using Equation 3.1.[22, 34]

$$Shrinkage(\%) = \frac{\Delta L_1}{L_0} \times 100 \qquad (3.1)$$

Residual shrinkage is the remaining changing length after the initial shrinkage test (L_2), while the sample remains in the conditioned environment and pre-tension is maintained. This can be obtained by applying Equation 3.2.[22,34]

$$Residual\ Shrinkage(\%) = \frac{\Delta L_2}{L_0} \times 100 \qquad (3.2)$$

It is equally possible to measure shrinkage-force and residual shrinkage-force, forces that occur due to the exposure of the sample to temperature changes and pre-tension during a specified time frame. As explained previously, residual shrinkage-forces are obtained during the second stage of the test when the sample is exposed to a conditioned environment.[22,34]

Twist

A yarn or cord from a spool or textile fabric is used as a test sample. This sample must not be damaged and be handled in order to avoid any changes in twist. At least 0.5 m of material should be discarded between measurements. The number of turns and the twist direction are determined by untwisting using a Mensdanlab Untwister (Figure 13), according to ISO 2061. Tree measurements were performed to each cord and yarn to ensure the cords were twisted correctly.[22,35]

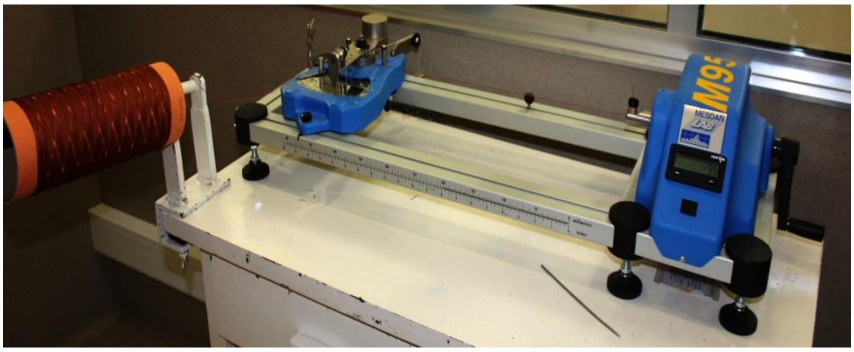

Figure 13- Electronic Twist Tester

Pre-tension is applied to the cord and then the movable clamp is turned against the twist direction of the cord until the single filaments or yarns are parallel to the cord axis. A clamping length of 500 mm is applied. Just as for other tests, the pre-tension applied to the sample is obtained by adding the decitex of the yarns, then multiplying for the number of plies and then multiplying the cord construction by 0.05. For example, in a nylon 940 dtex cord, with a 2 ply construction, the pre-tension applied should be as shown in Equation 3.3.[22, 35]

$$pre-tension = 940\ dtex \times 2\ plys \times 0.05 = 94\ cN \tag{3.3}$$

First, the cord is untwisted in the *s* direction. When untwisted, all plies but one should be cut from the sample in order to measure the twist of the yarn in the *z* direction. The pre-tension should be altered according to the specified above. The yarns are untwisted in the *z* direction until the filaments are parallel. A needle can be used to separate the filaments and when the needle can be moved from one clamp to the other, parallelism is obtained and the test is finalized.[22,35]

Ply difference

For this test method, 1 meter long samples are taken, discarding some meters in between samples. The cords are untwisted to separate plies and then their length is individually measured. The difference in length between plies constitutes ply difference. For most cords, the maximum limit established is 15 mm with the exception of hybrid cords.[11]

Tree samples were taken to ensure ply difference was within the maximum limit established. All the cords out of the limit established were replaced by re-twisting new spools using the correspondent greige yarn spools.[11]

Peel Adhesion Test

Static adhesion test was performed an average of three times, according to ASTM D4776. As previously stated, this method covers the determination of peel adhesion of reinforcement materials that are bounded to rubber compounds and it is applicable to either woven or parallel cords, textile structures from both natural and man-made fibers and parallel steel cord structures.[22,36]

After assembling the test specimen, the following step is vulcanization. The test specimen is then cut into 25 mm straps in the long direction parallel to the direction of the cords. After vulcanization, the specimen is conditioned for at least 3 hours and then heated for 30 minutes at 120 ºC. The peel adhesion test must be performed immediately after heating the samples. Each specimen is then individually placed and grasped separately by the clamps of the tensile testing machine. One of the clamps of the tensile tester is fixed while other moves at constant speed, pulling one half of the specimen. The force is registered through the tensile tester and the average value obtained is the corresponding peel force.[21, 22]The tensile tester is represented in Figure 14.

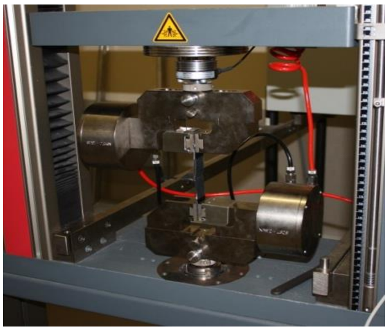

Figure 14- Tensile testing machine with peel adhesion test clamps

After the peel test it possible to qualify the specimen according to the coverage of the cords. This parameter is called appearance or coverage. It can vary from 1 to 5; one being the cords can be seen almost without any rubber compound on top and 5 a specimen totally covered by the rubber compound.

Gage Repeatability and Reproducibility Study

The main focus of this study is to determine the accuracy of the measurement system. The tested variables chosen were peel force and load-elongation (elongation at break and maximum elongation). Although this type of method is meant to be applied to non-destructive samples, it was considered valid to apply this method for this is meant to be a preliminary study. Of all the different types of Gage R&R studies, crossed Gage R&R seemed more appropriate since it estimates the variation caused by part-to-part variation and measurement system (repeatability and reproducibility and method) variation.[30] This study was accomplished using both *Minitab Statistical Software*® and *R*®.

4 Results and Discussion

The present dissertation is divided in two distinct analysis. Firstly, repeatability conditions were respected in order to characterize and analyze 30 spools of each material tested. This allowed the determination of how many samples were required to test and also allowed the comparison of standard deviations and averages between parameters. Secondly, operators and parts were changed in order to assess the variation of the same methods when compared to the previous study and also compare consistency between operators.

4.1 Distribution and precision analysis

As said before, the first stage of this study includes a detailed study of 30 spools of nylon 940. After, the same study on a different material, PET 1440, was performed in order to compare the results obtained between the two materials.

As previously stated, all results were treated using the *Shapiro-Wilk* test of normality. This test helps to determine if the initial assumption that the 30 spools tested follow a normal distribution regarding all test methods. A confidence level of 95 % and a margin of error up to 5 % of the sample mean were established to define all the unknown parameters. The result of the sample size (*n*) required was obtained using Equation 2.1 and, in this case, refers to the number of spools.

For multiple parameters tests, the results of the parameter that requires the higher number of samples to test is shown and discussed on the following chapter. For all the other tests the results are given in Annex II.

Linear Density

Linear density (expressed in dtex) is one of the specifications provided by the yarn supplier. This test is performed as a confirmation test to some of the spools delivered at C-ITA. On the other hand, for dipped cords there is a specification for weight per length previously established. The results of yarn dtex regarding nylon 940 and PET 1440 are in Table 4.

Table 4-Results of yarn dtex for nylon 940x1x2 and PET 1440x1x2

	$\overline{X}_{dtex}$ / g×10 000 m^{-1}	*S* / g×10 000 m^{-1}	S^2 / (g×10 000 m^{-1})^2	*W-value*	*p-value*
Nylon 940	914.23	4.92	24.19	0.93	0.061
PET 1440	1449.00	15.30	234.09	0.95	0.162

Regarding nylon 940 yarns, the average of the sample value is low when compared to the established by the supplier (940 dtex).The same was not verified for PET 1440 were the value specified by the yarn supplier is much closer to the obtained average value. *p-value* is lower for nylon 940 than for PET 1440 but still within the established limits so, for both cases, normality may be considered. From the analysis of the probability plots (Figure 15) it is possible to see some deviations that justify the low *p-values* obtained for nylon.

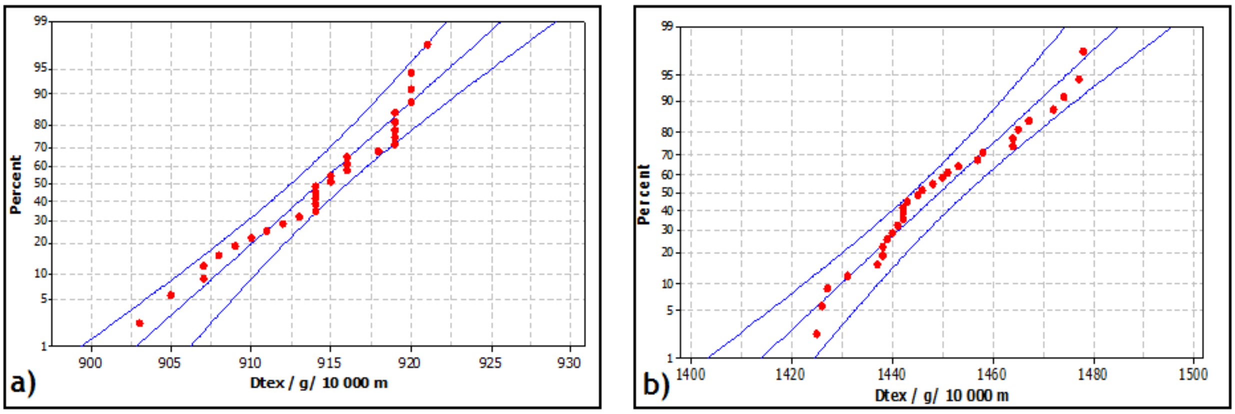

Figure 15- Probability plot of yarn dtex for nylon 940 (a) and PET 1440 (b).

For greige cords there are no established limits. The obtained results are shown in Table 5.

Table 5- Results of greige cords dtex for nylon 940x1x2 and PET 1440x1x2

	$\overline{X}_{dtex}$ / g×10 000 m^{-1}	S / g×10 000 m^{-1}	S^2 / (g×10 000 m^{-1})^2	W-value	p-value
Nylon 940	1944.33	5.59	31.26	0.95	0.150
PET 1440	3141.00	22.96	527.16	0.95	0.167

From Table 5 it is possible to conclude that the greige cords dtex data show a good fit to the normal distribution. For greige nylon 940 cords the probability plot distribution (Figure 16) displays some tendency values (grouped data) and some dispersed higher and lower values when compared to the average values. For greige PET cords, the probability plot (Figure 16) also displays dispersed data on the extremities of the plot.

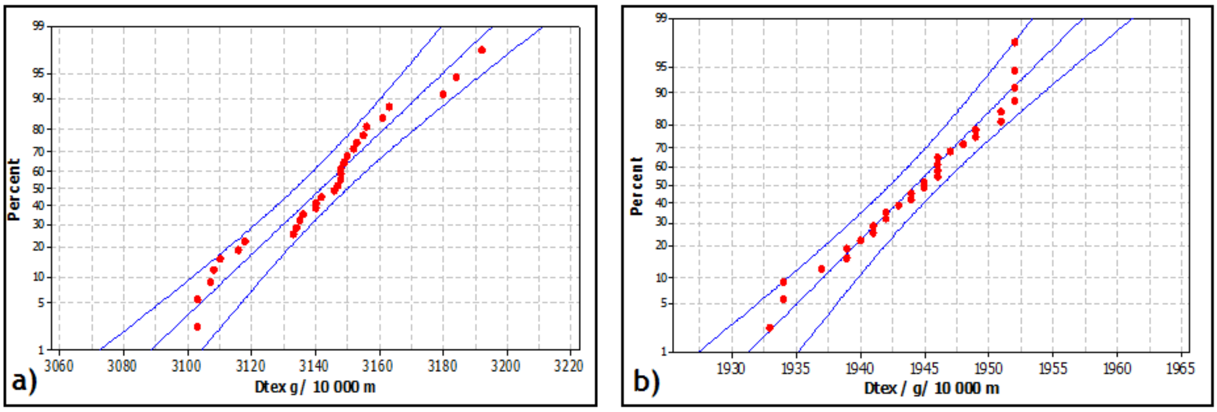

Figure 16- Probability plot of the results for nylon 940 (a) and PET 1440(b) greige cords dtex

The box plots (Figure 17) indicate that for both materials the data is spread due to the length of the whiskers, although for nylon 940 the median is more balanced dividing equally both quartiles. For PET 1440, the box plot displays an outlier, a value that is far from all the other obtained values. An outlier may be an indicator of the variability of the method, experimental error or also be related to inconsistency between spools.

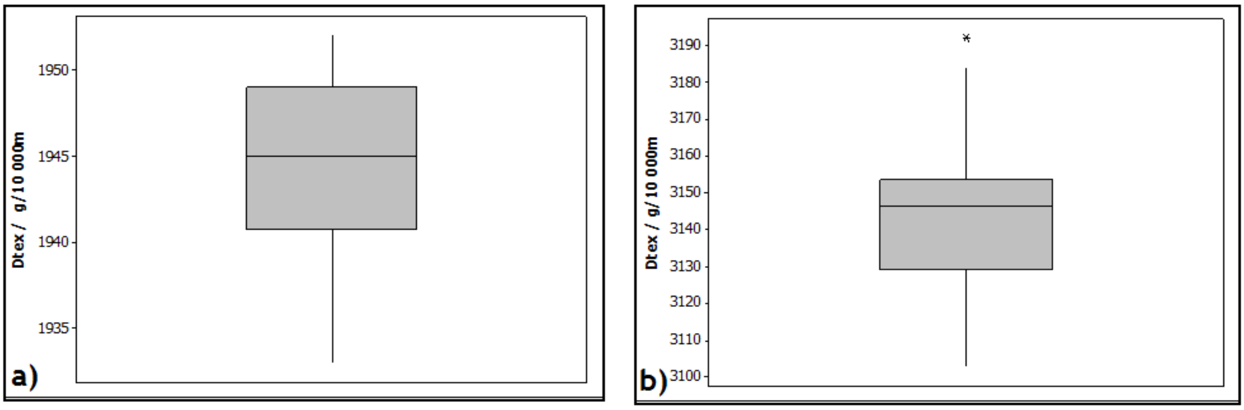

Figure 17- Box Plots for nylon 940 (a) and PET 1440 (b) greige cords dtex

The results in Table 6 show that the assumption of normality is correct.

Table 6-Results of weight per length of dipped cords for nylon 940x1x2 and PET 1440x1x2

	$\overline{X}_{dtex}$ / g×100 m^{-1}	S / g×100 m^{-1}	S^2 / (g×100 m^{-1})^2	W-value	p-value
Nylon 940	20.04	0.27	0.07	0.93	0.051
PET 1440	31.84	0.32	0.10	0.95	0.174

The probability plots of weight per length are in Figure 18. It is possible to observe that both distributions are similar. Unlike other parameters, weight per length displays data that can be qualified as discrete data. This can be confirmed due to the staircase pattern of the distributions that displays gaps and plateaus. For nylon 940 some values fall within the limit line and one value exceeds the limit line. That explains the low *p-value* obtained.

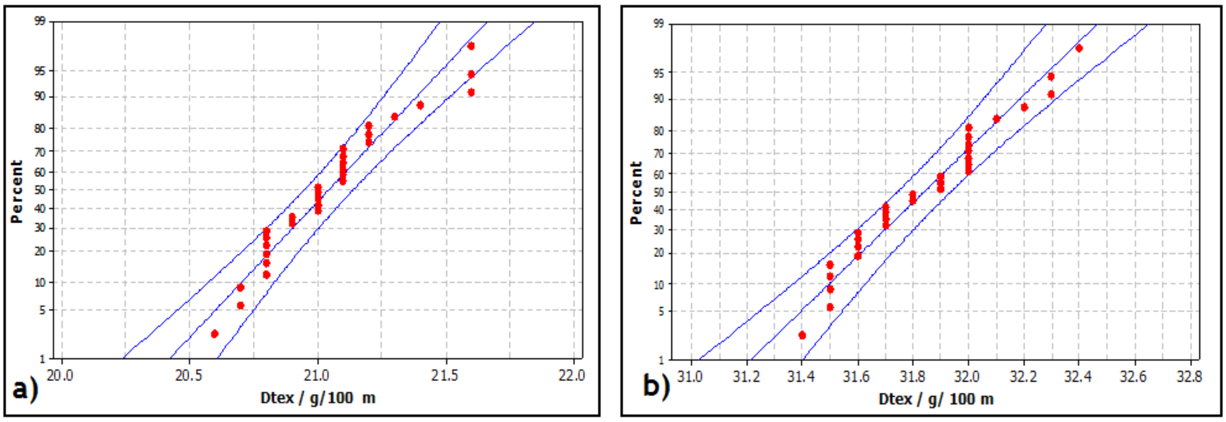

Figure 18- Probability plot of the results for nylon 940 (a) and PET 1440 (b) dipped cords dtex

The data presented regarding all linear density testing procedures indicates that one sample is required, for a 95 % confidence level and margin of error up to 5 % of the sample average Linear densities results display similarities between fibers and also indicate that the method complies with the precision required.

Thickness

To all states of the yarn/cord thickness was measured although the method is validated for dipped cords. Regarding nylon 940, the results are presented in Table 7.

Table 7- Thickness for nylon 940x1x2 in all stages of the manufacturing process

	$\overline{X}_{\text{thickness}}$/ mm	S / mm	S^2 / mm^2	*W-value*	*p-value*
Yarn	0.134	0.012	1.03×10^{-2}	0.97	0.586
Greige Cord	0.430	0.027	2.52×10^{-2}	0.94	0.098
Dipped Cord	0.560	0.015	1.51×10^{-2}	0.97	0.424

The results in Table 7 indicate that normality can be assumed for a confidence limit of 95 % and margin of error defined. As expected, the sample mean varies according to the state of the cord. For PET 1440, the results are presented in Table 8.

Table 8- Thickness results for PET 1440x1x2 in all stages of the manufacturing process

	$\overline{X}_{\text{thickness}}$/ mm	S / mm	S^2 / mm^2	*W-value*	*p-value*
Yarn	0.161	0.013	1.22×10^{-2}	0.81	0.233
Greige Cord	0.550	0.025	2.12×10^{-2}	0.98	0.702
Dipped Cord	0.631	0.011	1.15×10^{-2}	0.96	0.252

In this test, greige cords of both materials show higher deviations when compared to the thickness measured of yarns and dipped cords. This can be explained because the method is harder to perform to cords in this state. Avoiding loss of twist and not overlapping the cords is very hard to accomplish. The normalized plots for the different states of yarn /cord are displayed in Figure 19, Figure 20 and Figure 21.

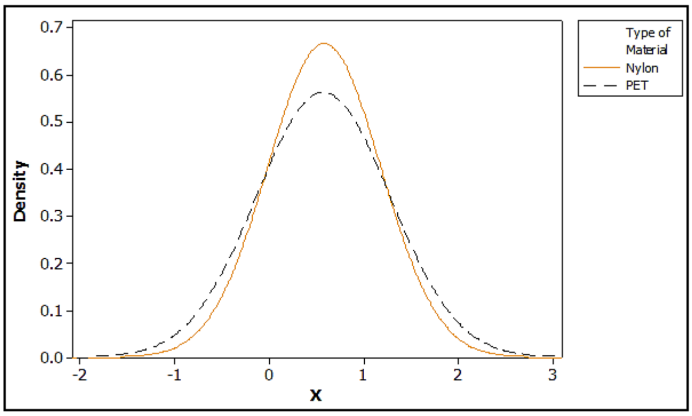

Figure 19- Normalized distribution plot of yarn thickness for the tested fibers

In Figure 19 it is possible to observe that nylon 940 exhibits smaller deviations when compared to PET 1440. Furthermore, the normalized thickness sample mean for nylon 940 is higher when compared to PET 1440. This might indicate that differences between the distribution obtained is higher for nylon than for polyester.

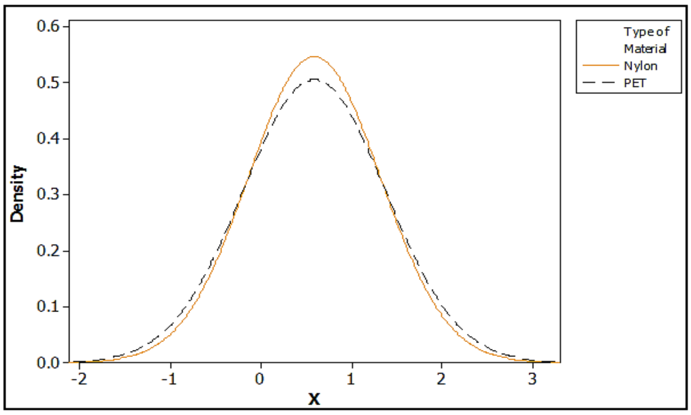

Figure 20- Normalized distribution plot of greige cords thickness for the tested fibers

For greige cords the normalized results are very similar for both materials. The normalized results for dipped cords (Figure 21) show the highest differences between the materials. This indicates that the differences between maximum and minimum values are lower for PET 1440 than for nylon 940.

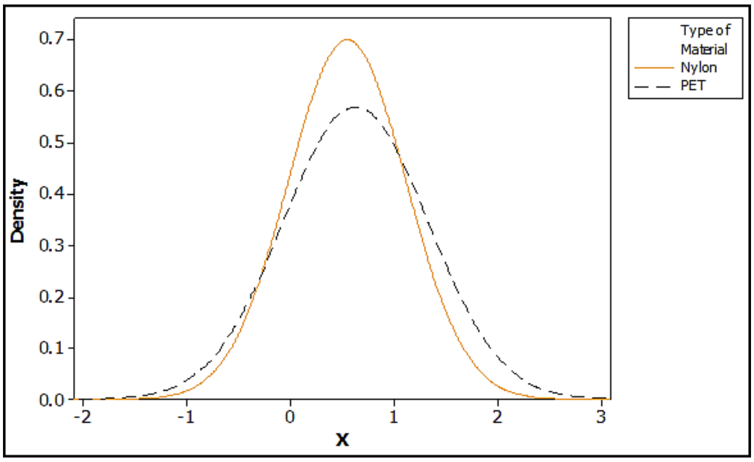

Figure 21- Normalized distribution plot of thickness of greige cords for the tested fibers

The number of samples to test in order to ensure thickness results for all states of yarn/cord regarding both materials tested is presented in Table 9.

Table 9- Number of samples required for both materials tested

	Yarn	Greige Cord	Dipped Cord
Nylon 940	13	7	1
PET 1440	10	4	1

The results in Table 9 indicate that the number of samples required regarding yarns is very high when compared to the results obtained for dipped cords. This might be an indicator of the reason why this test is only validated for dipped cords. The results indicate that this method should be revised according to linear densities. For higher linear densities the placement of four cords in a row is unviable since there is high probability of overlapping the cords and exceeding the capacity of the measuring device with diameter of 10 mm. Also, since the number of repetitions for each spool was increased in relation to the established test method, repeatability and reproducibility should be studied in detail. For these reasons, this test method does not comply with the required precision.

Twist Level

As said before, the correct twist of yarn and cord is a really important quality to confirm, since it ensures some of the most important characteristics of the cord. Before the dipping process, loss of twist in the samples taken has major influence on the results. On the other hand, after the dipping process the cords are stiffer becoming more difficult to measure twists. For all cases, the data are discrete and not continuous and this fact can be confirmed by the observation of the probability plots.

Yarn Twist

The results obtained for nylon 940 and PET 1400 yarns are in Table 10.

Table 10-Yarn twist results for PET 1440x1x2 and nylon 940x1x2

Type of Material:	State of the yarn:	$\overline{X}_{yarn\ twist}$/ tpm	S / tpm	S^2 / tpm^2	W-value	p-value
Nylon 940	Greige	346	6	36	0.96	0.338
	Dipped	339	4	19	0.96	0.411
PET 1440	Greige	377	5	25	0.95	0.197
	Dipped	369	2	6	0.96	0.233

From Table 10, it is possible to observe that *p-values* and *W-values* are very high so, for both materials, it is possible to consider that the distribution fits the normal distribution. The probability plots demonstrate similarities in behaviors. Most values are grouped but both cases display some spread values and values that are almost beyond the limits established.

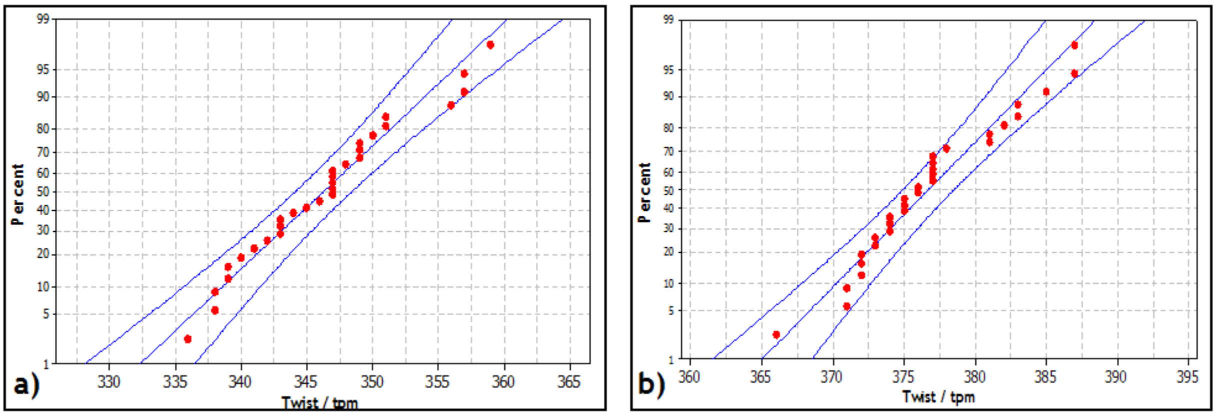

Figure 22- Probability plot of greige yarn twist for nylon 940 (a) and PET 1440 (b)

Figure 23 displays the same type of distribution, with grouped data and a few values spread from the center.

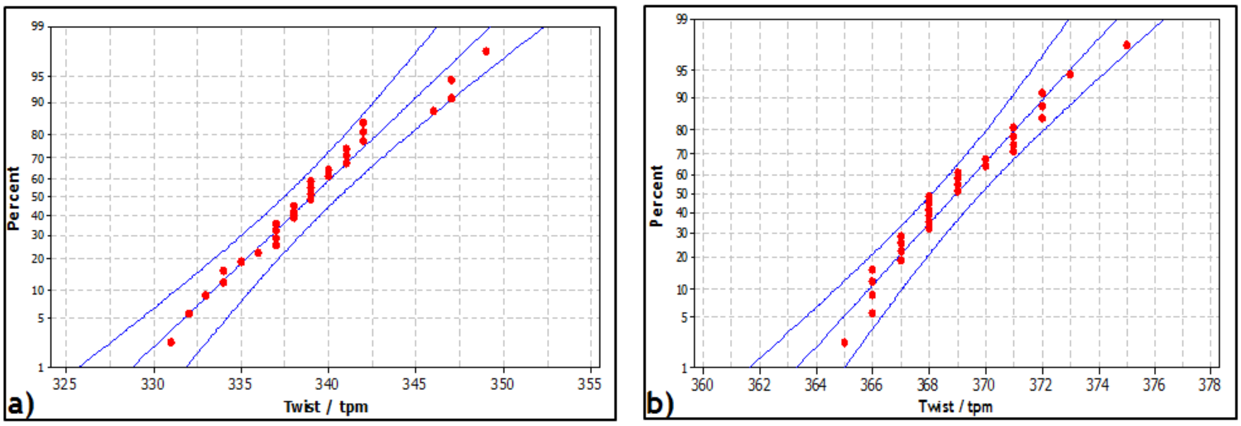

Figure 23- Probability plot of dipped yarns twist for nylon 940 (a) and PET 1440 (b)

The box plots of the distribution of dipped yarns (Figure 24) help the characterization of the results. For nylon 940, the box plot displays outliers but a balanced median since it divides the first and third quartile equally. It can be observed, by the length of the whiskers on the box plots that the lowest and highest values are spread from most of the values obtained. For PET 1440 the median is not at the center but the results do not display outliers.

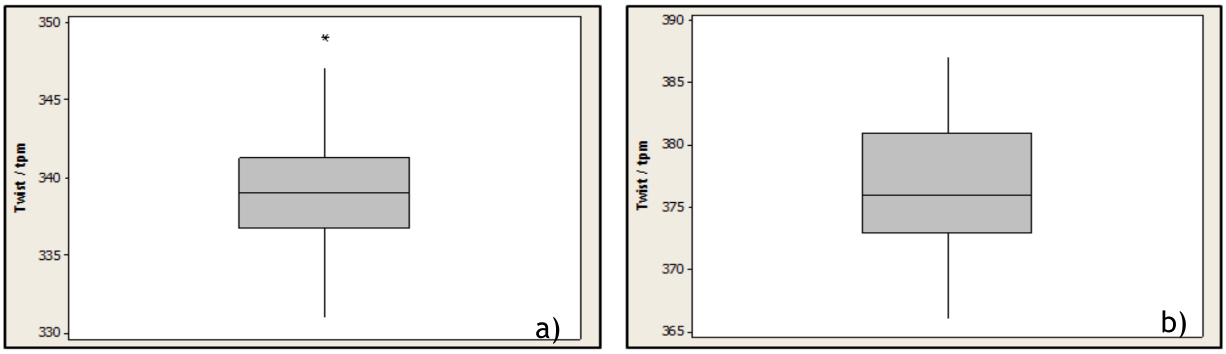

Figure 24 - Box plots of yarn twist for nylon 940 (a) and PET 1440 (b)

Cord Twist

The results obtained for cord twist are similar to yarn twist, both in averages and deviations. The results are presented in Table 11.

Table 11- Cord twist results for PET 1440x1x2 and nylon 940x1x2

Type of Material:	State of the cord:	$\bar{X}_{cord\ twist}$/ *tpm*	*S / tpm*	*S^2 / tpm^2*	*W-value*	*p-value*
Nylon 940	Greige	343	6	36	0.97	0.424
	Dipped	340	5	21	0.97	0.420
PET 1440	Greige	367	5	29	0.95	0.169
	Dipped	359	2	4	0.94	0.110

In Table 11, it is possible to conclude that the deviations are higher for greige cords than for dipped cords. The results for the assumption of normal distribution are satisfactory, displaying high *p-values* and *W-values*. The probabilities plots are on Figure 25 and Figure 26.

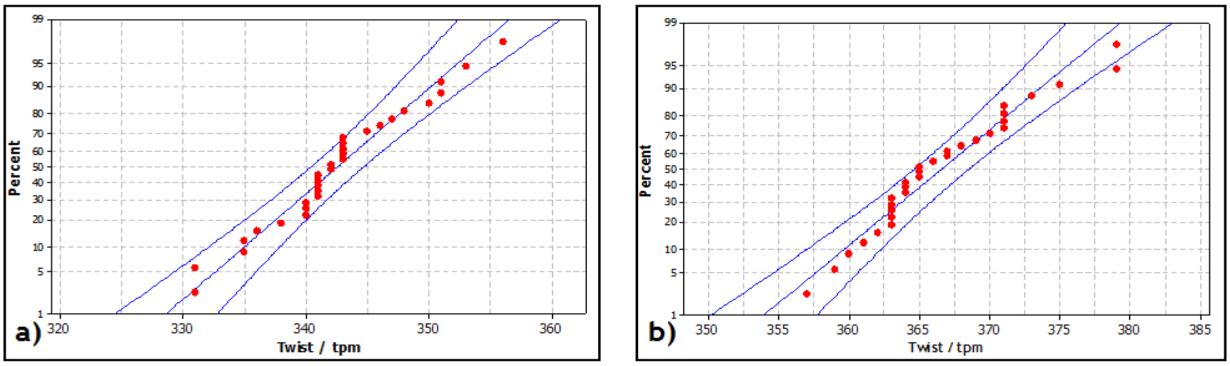

Figure 25- Probability plot of greige cords twist for nylon 940 (a) and PET 1440 (b)

Nylon greige cords twist display the highest variation but similar to yarn twists it displays grouped data. PET 1440 distribution is more spread than others displaying values between the higher and lower limits established.

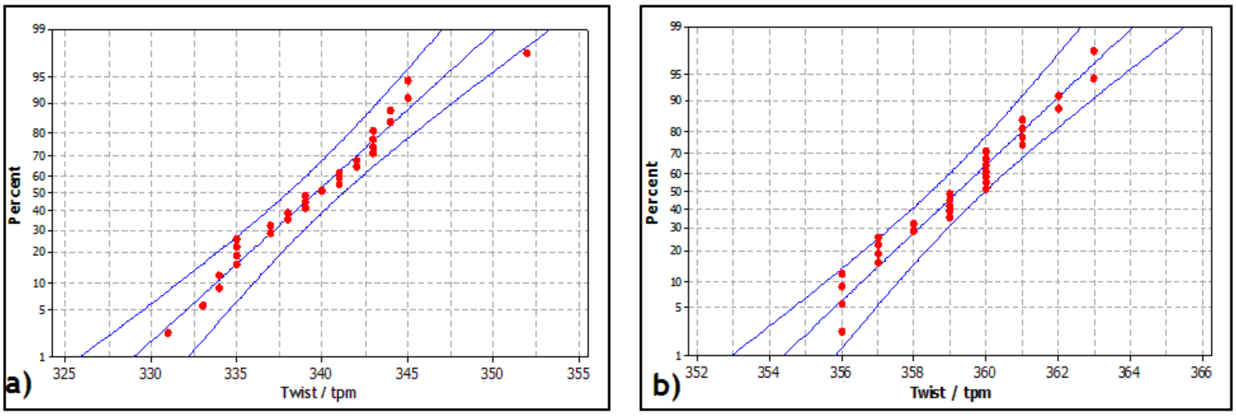

Figure 26- Probability plot of dipped cords twist for nylon 940 (a) and PET 1440 (b)

Regarding PET 1440, there are noticeable similarities between the probabilities plot for yarn and cord twist. Nylon 940 does not display the same the same tendencies. Since the methods of testing are the same, these tendencies are probably related to the properties of the fibers.

The application of Equation 2.1 results in one sample for both cord twists and yarn twists regarding both materials tested. This result is easily explained by the low deviation values presented when compared to the established and obtained means. It can be established that this test method complies with the required precision and that in this case the type of fiber does not seem to greatly influence the results.

Ply Difference

Ply difference is measured typically in greige cords. The results obtained are in Table 12.

Table 12- Ply difference results for PET 1440x1x2 and nylon 940x1x2

	$\overline{X}_{Ply\ Difference}$ /mm	*S / mm*	*S^2 / mm^2*	*W-value*	*p-value*
Nylon 940-Greige cord	4	2	6	0.95	0.157
PET 1440-Greige cord	3	2	6	0.93	0.053

From the observation of the table above, it is possible to conclude that for both materials the standard deviation is very high when compared to the sample mean obtained. For these tests it is useful to visualize the histograms since the distributions are non-symmetric (Figure 27).

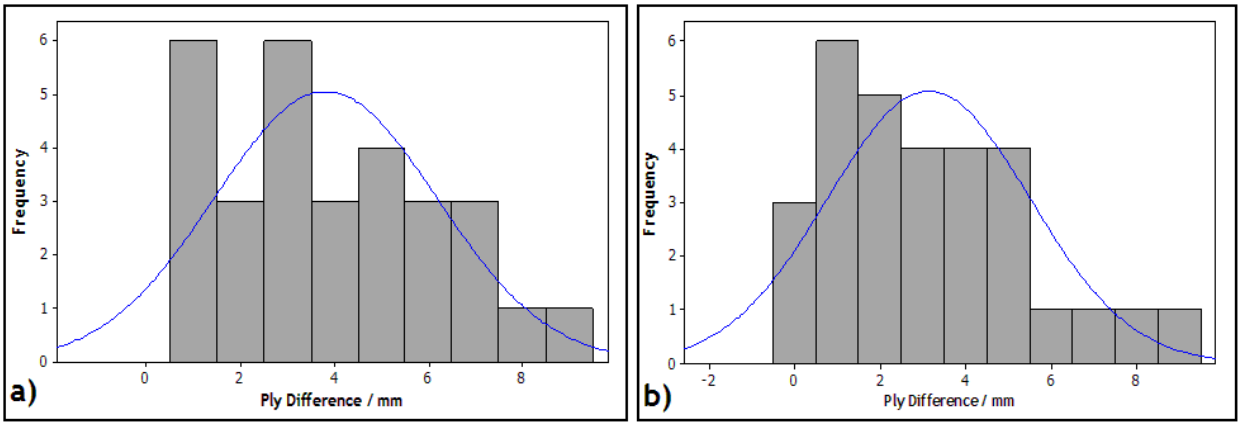

Figure 27- Histogram of the results of ply difference for nylon 940x1x2 (a) and PET 1440x1x2 (b)

A statistical analysis concluded that both distributions are moderately skewed to the right, indicating that the right tail is long when compared to the left tail. These distributions also display kurtosis. In an ideal normal distribution there is neither skewness nor kurtosis so this may be an indicator that even if *p-values* and *W-values* are in the accepted ranges the distributions may not be normal. Nevertheless the normalized distribution plot assuming the normal distribution is displayed in Figure 28.

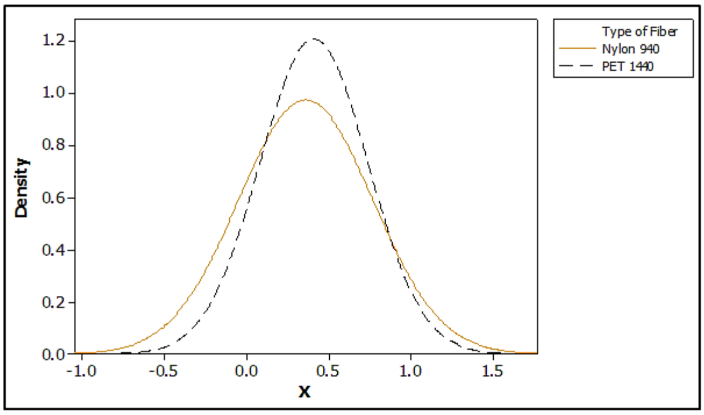

Figure 28- Normalized distribution plot of ply difference for the tested fibers

Since the standard deviation of this test method is high when compared to the sample mean, the results obtained from the application of Equation 2.1 indicate that a very high number of samples would be required; more than 500 spools for each material. For this reason, this test will not be considered fit for its purpose is regarded as a qualitative test rather than a quantitative test.

Load-Elongation

As said before, load-elongation curves provide important information about the cord. Besides breaking strength, for nylon cords there are also limits established for force at 2 % and 4 % elongation.

In general, for both materials tested, the parameter that displayed higher deviation in this test method in relation to the average value was maximum elongation. This value is obtained by difference between initial and final (at break) elongation and is expressed as a percentage. The results obtained for nylon 940 are displayed in Table 13.

Table 13- Load-Elongation (Maximum Elongation) results for nylon 940x1x2

	$\overline{X}_{Load\ Elongation}$/%	S / %	S^2 / %	W-value	p-value
Yarn	16.82	0.44	0.19	0.96	0.309
Greige Cord	20.84	0.78	0.62	0.97	0.456
Dipped Cord	19.78	0.91	0.83	0.97	0.421

From Table 13, it is possible to observe that the deviations obtained are very low when compared to the average. On the other hand, *p-values* and *W-values* are very high clearly stating that all the distributions can be considered normal distributions.

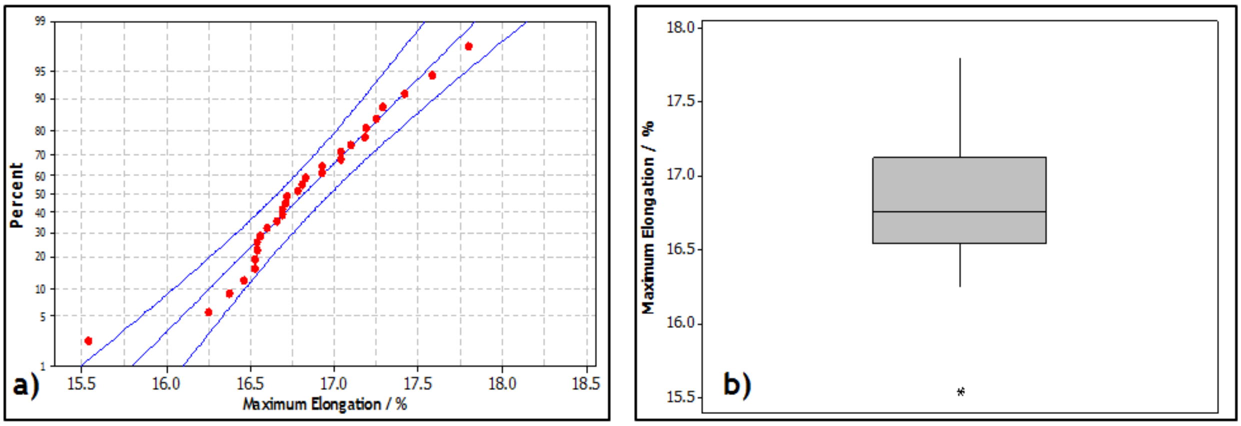

Figure 29 - Probability plot (a) and box plot (b) of load-elongation for nylon 940 greige yarns

Figure 29 clearly justifies the *p-value* and *W-values* obtained. It is possible to observe that there is an outlier; this is confirmed by observing the box plot. The whiskers are longer in one side than the other and the median is closer to the first quartile nevertheless normality is assumed. The probabilities plot for nylon 940 greige cords and dipped cords are presented in Figure 30.

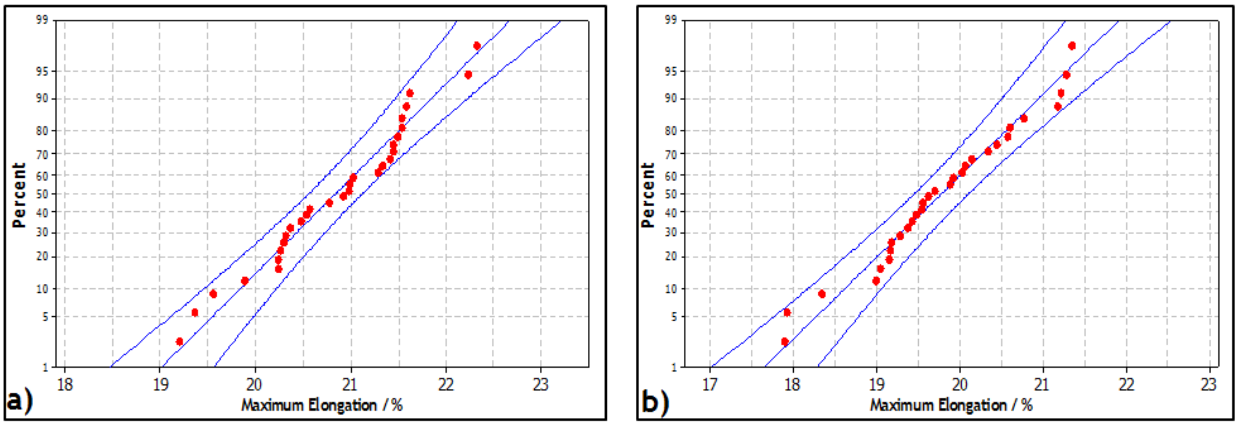

Figure 30- Probability plot of load-elongation for nylon 940 greige (a) and dipped cords (b)

The probability plots for greige and dipped nylon 940 cords do not indicate the presence of outliers. Both cases show some values that deviate from the center line but do not exceed the limits established.

For PET 1440 yarns and greige cords, the parameter that required testing a higher number of samples was maximum elongation. However, for dipped cords the results differed from the previous ones, indicating that the parameter with highest deviation in relation to the mean was elongation at 20 N. The main results from the load-elongation tests are in Table 14.

Table 14- Load-Elongation results for PET 1440x1x2

	$\overline{X}_{Load\ Elongation}$ / %	S / %	S^2 / %	W-value	p-value
Yarn (Elong@Max)	11.45	1.54	2.38	0.95	0.210
Greige Cord (Elong@Max)	16.25	0.63	0.39	0.96	0.271
Dipped Cord (Elong@20N)	0.92	0.06	3.22×10^{-3}	0.97	0.657

The results for PET 1440 with the exception of dipped cords display lower *p-values* and *W-values* nevertheless the established conditions are fulfilled. The probability plots provide a better indication of the reason why these results differ from nylon 940 (Figure 31).

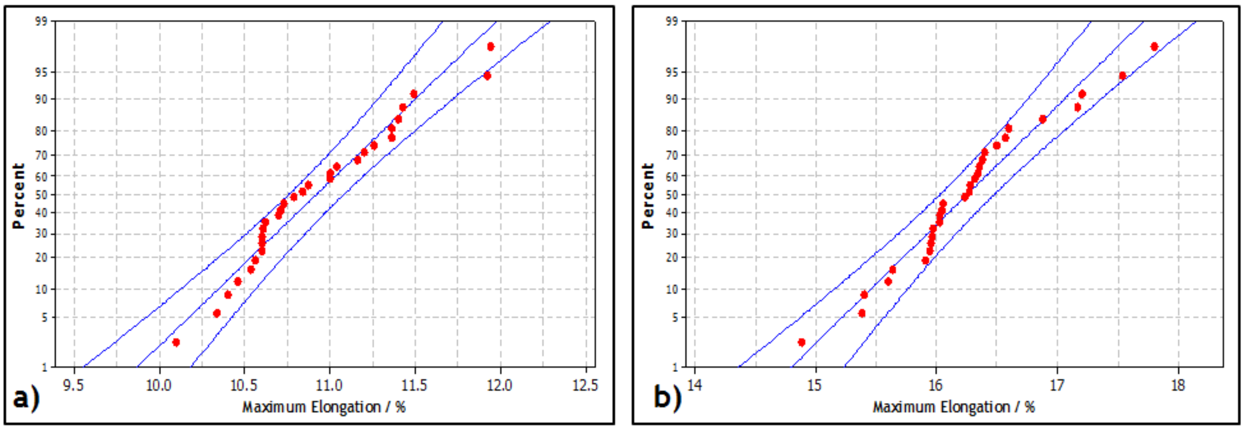

Figure 31- Probability plot of load-elongation for PET 1440 greige yarns (a) and greige cords (b)

The probability plot for PET 1440 greige cords does not display outliers but the observation of the box plot (Figure 32*)* indicates the presence of outliers, superior and inferior to the median. However, the median is balanced, dividing equally both quartiles. The inter-quartile distance is not very high which indicate that the values are close among themselves.

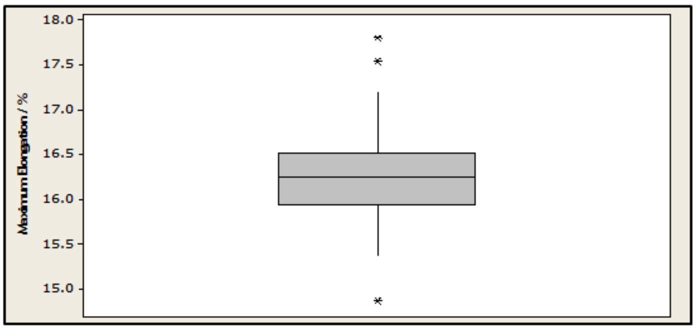

Figure 32- Box plot for load-elongation for PET 1440 greige cords

The probability plot for load-elongation results of PET 1440 is presented o*n* Figure 33. This probability plot indicates that the distribution of the sample mean is a good fit to the normal distribution.

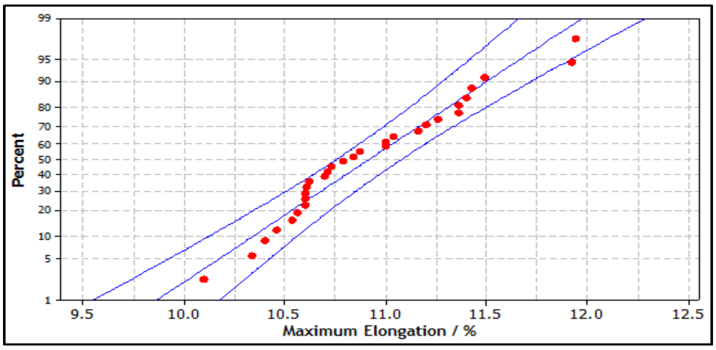

Figure 33- Probability plot of load-elongation for PET 1440 dipped cords

This test method displays differences in the number of samples (spools) required to test for each stage of the manufacturing process and also differences between materials. The main results are in Table 15.

Table 15- Number of samples required to test to guarantee load-elongation results for both materials tested in each stage of the manufacturing process

	Nylon 940	PET 1440
Yarn	1	2
Greige Cord	3	3
Dipped Cord	1	5

These results indicate that the type of fiber influences the number of samples required to test. Unlike other test methods, the deviations when compared to the average value are higher for PET than for nylon thus requiring a higher sample size.Nevertheless, these results indicate that this method complies with the required precision.

Thermal Shrinkage

Regarding nylon 940, all the results presented result from the effective thermal shrinkage. Nevertheless all the results before and after the dipping process are within the standardized limits. The main results for thermal shrinkage for both materials tested are presented in Table 16.

Table 16- Thermal Shrinkage for PET 1440x1x2 and nylon 940x1x2

		$\overline{X}_{Thermal\ Shrinkage}$ /%	*S / %*	S^2	*W-value*	*p-value*
Nylon 940	Yarn	4.97	0.34	0.12	0.95	0.155
	Dipped Cord	4.69	0.28	0.078	0.97	0.414
PET 1440	Yarn	4.78	0.30	0.090	0.98	0.821
	Dipped Cord	3.85	0.20	0.040	0.98	0.803

As previously stated thermal shrinkage has two parameters: efective shrinkage and residual shrinkage. In Table 16 only effective thermal shrinkage results are shown. It is possible to observe that although the materials are very different regarding its amorphous structure, higher for nylon than for polyester fibers, sample means and deviations are more similar than expected. The statistical results for normal distribution are very satisfatory, displaying high *p-values* and *W-values*. This can be confirmed by the observation of the distribution plots (Figure 34, Figure 35 and

Figure 36).

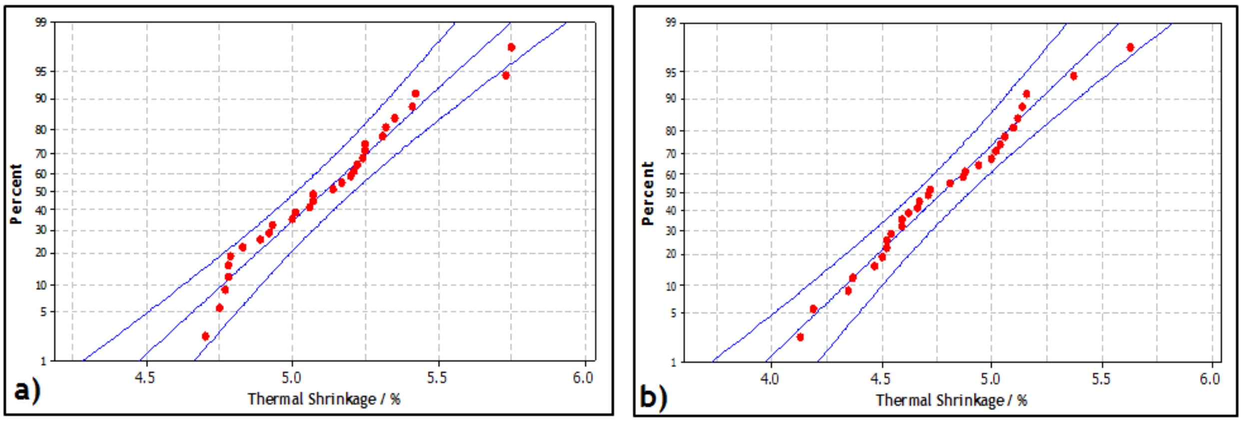

Figure 34 - Probability plot of effective thermal shrinkage nylon 940(a) and PET 1440 (b) greige yarns

As said before, unlike other test methods, thermal shrinkage distributions are very similar for both materials tested. Both distributions present two values that are further from the expected values of a perfectly normal distributions; nevertheless,normality can be assumed.

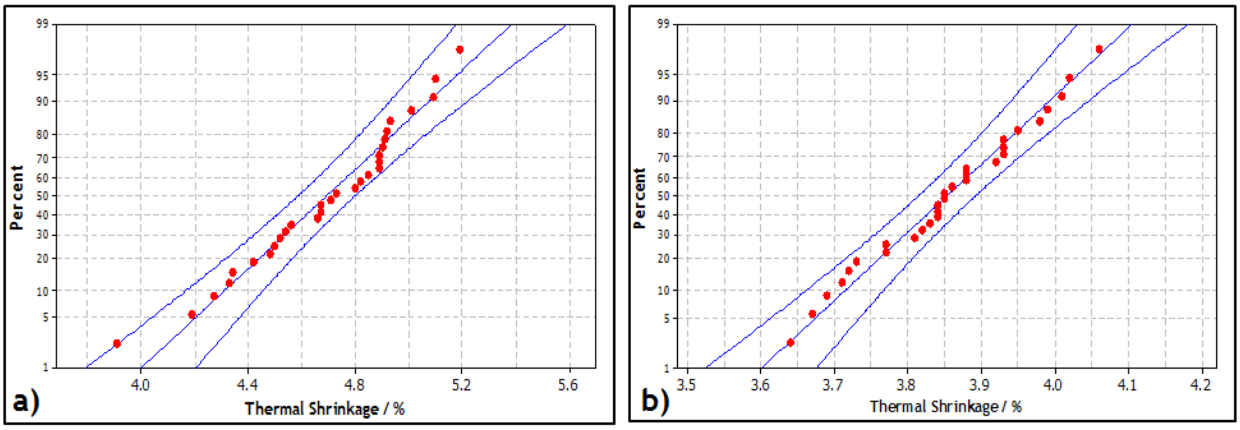

Figure 35- Probability plot of effective thermal shrinkage nylon 940 (a) and PET 1440 dipped cords (b)

Regarding dipped nylon 940 cords (Figure 35) the distribution displays the lowest value almost in the established limits. For PET 1440, the spools tested result in a close fit to the normal distribution with few deviations from the straight line.

The results of these test methods for both fibers, with the required number of samples (spools) to test are in Table 17.

Table 17- Number of samples required to rest for each material regarding thermal shrinkage

		Required Number of Spools
Nylon 940	**Yarn**	8
	Dipped Cord	6
PET 1440	**Yarn**	6
	Dipped Cord	4

For PET 1440 the test method proves to demand a smaller sample size due to the characteristics of the fiber. Therefore the obtained number of spools should be respected in order to guarantee the results.

Thermal Shrinkage-force

For shrinkage-force, different parameters will be considered for both fibers due to the results For nylon 940 effective thermal shrinkage-force is considered and for PET 1440 effective thermal shrinkage-force is presented. The results regarding nylon 940 are in Table 18.

Table 18- Effective Thermal Shrinkage-force for nylon 940x1x2

	$\overline{X}_{T.Shrinkage-force}$ /N	S / N	S^2 / N^2	*W-value*	*p-value*
Yarn	287.95	5.90	34.84	0.98	0.805
Dipped Cord	529.24	1.38	1.91	0.98	0.722

It is possible to observe that in both cases, the deviations are small when compared to the sample mean. The *p-values* and *W-values* are very high and it is possible to observe by analyzing the probability plots (

Figure 36) that normal distribution can be assumed.

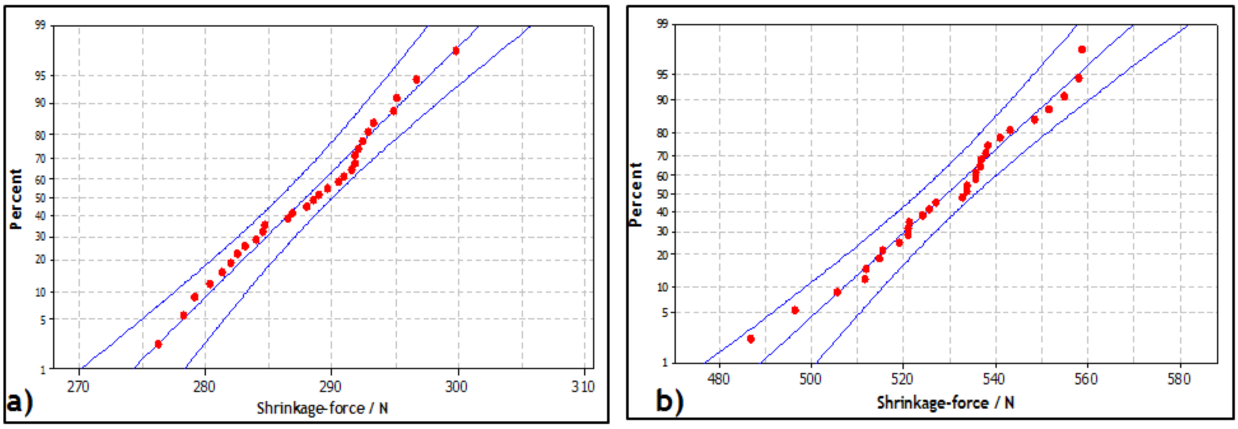

Figure 36-Probability plot of effective thermal shrinkage-force for nylon 940 greige yarns (a) and dipped cords (b)

In Table 19, the results of residual shrinkage for PET 1440 are presented.

Table 19- Residual Thermal Shrinkage-force for PET 1140x1x2

	$\overline{X}_{T.Shrinkage-force}$ /N	S / N	S^2 / N^2	*W-value*	*p-value*
Yarn	219.84	9.56	91.39	0.94	0.086
Dipped Cord	342.54	17.73	314.20	0.98	0.688

Regarding residual thermal shrinkage-force for PET 1440 yarns, the *p-value* obtained is low when compared to the others obtained for this test. This can be easily explained by the observation of the probability plot (Figure 37).

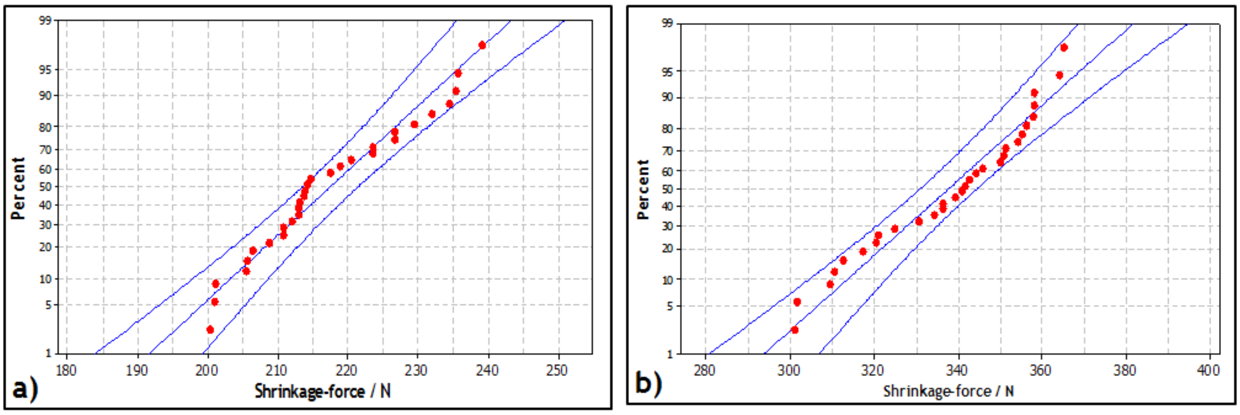

Figure 37- Probability plot of residual thermal shrinkage –force for PET 1440 greige yarns (a) and dipped cords (b)

Although the ranges are not similar, residual thermal shrinkage for PET 1440 dipped cords display similar distributions. The obtained *p-value* and *W-value* allow the approximation of the data to the normal distribution.

Table 20- Number of spools required to rest for each material regarding thermal shrinkage force

		Required Number of Spools
Nylon 940	Yarn	1
	Dipped Cord	1
PET 1440	Yarn	3
	Dipped Cord	4

The higher standard deviation when compared to the average mean for PET 1440 requires testing a higher number of spools. Furthermore, the evaluated parameters were different, effective thermal shrinkage-force for nylon and residual thermal shrinkage-force for PET result in different outcomes.

Nylon 940: Residual Thermal Shrinkage and Residual Thermal Shrinkage-force

Besides effective thermal shrinkage, residual thermal shrinkage is a part of the specification of the product for nylon. Although all the samples tested were within the established values (2.5 ± 0.7 %) the variations obtained are very high leading to a larger sample size. The same result was obtained for residual thermal shrinkage-force. The results are in Table 21 and Table 22.

Table 21- Main results for residual thermal shrinkage for nylon 940

	$\overline{X}_{\text{T.Shrinkage}}$/ N	S / N	S^2 / N^2	Number of spools
Yarn	3.19	0.28	0.078	12
Dipped Cord	2.50	0.18	0.032	8

Table 22- Main results for residual thermal shrinkage-force for nylon 940

	$\overline{X}_{\text{T.Shrinkage-force}}$/ N	S / N	S^2 / N^2	Number of spools
Yarn	10.46	4.52	20.43	287
Dipped Cord	8.20	5.40	29.16	670

From the analysis of the Tables 21 and 22, it is possible to see that this high number of samples required would be very hard to test within the industrial environment. Besides, these results are very different than the results obtained for PET 1440. The tests were performed with only a few weeks difference, using the same methodology and equipment which indicates that either the type of fiber or the supplier or both may influence this parameter on this test method. The difference in the crystallinity of the fibers could be the most influential factor and explain the differences in effective thermal shrinkage and shrinkage-force results when compared to the polyester. Nylon is less crystalline which can cause higher testing method variations than polyester. A detailed evaluation and assessment of the factors which may contribute to these results should be performed. Changing the materials, using different suppliers, evaluation of the equipment by comparing the results with other adequate equipment are some ideas to what can be done.

Peel Adhesion Test

The peel adhesion test is a complex and involves a multistage testing process. The average stress-strain curves for nylon 940 and PET 1440 are presented in Figure 38.

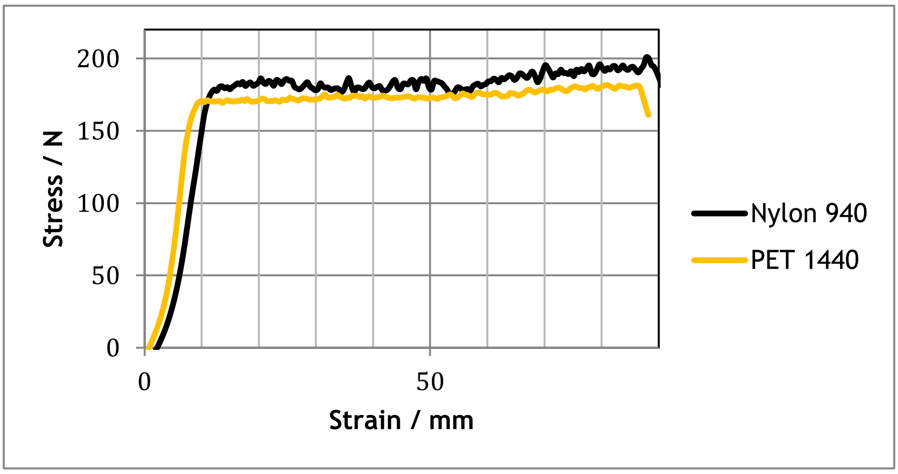

Figure 38- Average stress-strain curves for nylon 940 and PET 1440

The observation of Figure 38 indicates that the results are similar and in both cases the obtained peel force is superior to the minimum established (120 N). For these two products the dipping process is already developed. For this reason the appearances of the samples were always satisfactory and classified from 4.5 to 5.The peel adhesion results and statistical treatment are presented in Table 23.

Table 23- Peel Adhesion test results for nylon 940x1x2 and PET 1440x1x2

	$\overline{X}_{\mathbf{Adhesion}}$ /%	S / N	S^2/ N^2	*W-value*	*p-value*
Nylon 940 - Dipped Cord	197	5	23	0.98	0.844
PET 1440- Dipped Cord	178	4	16	0.98	0.781

The observation of Table 23 allows the conclusion that the approximation to the normal distribution is correct since both *w* and *p-values* are very high. The Q-Q plots confirm the statement above (Figure 39).

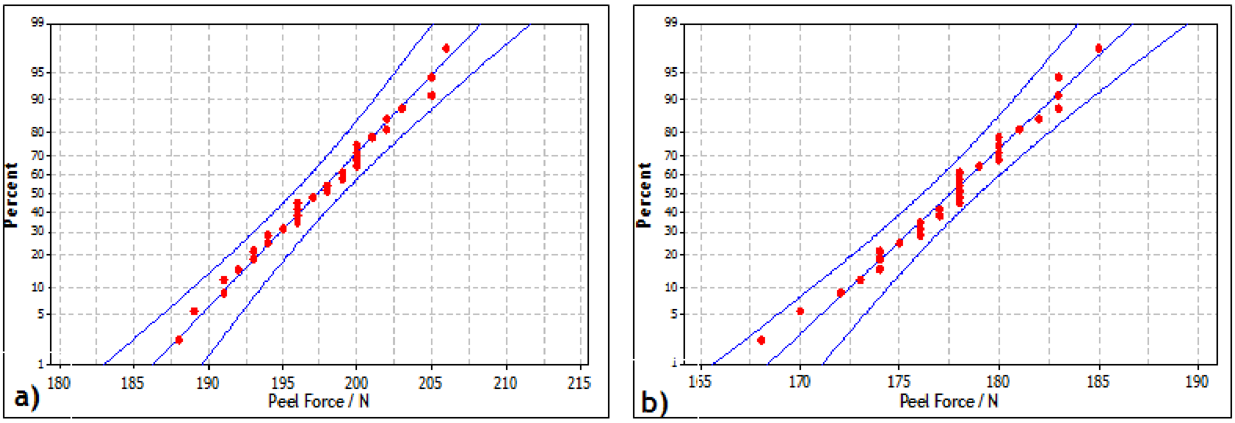

Figure 39- *Probability plot of the results of the peel force for nylon 940x1x2 (a) and PET 1440x1x2 (b)*

Unlike other test methods, the peel adhesion test results exhibited very similar behaviors when normalized. This can be better concluded after the observation of the normal distribution plot for the normalized peel forces (Figure 40).

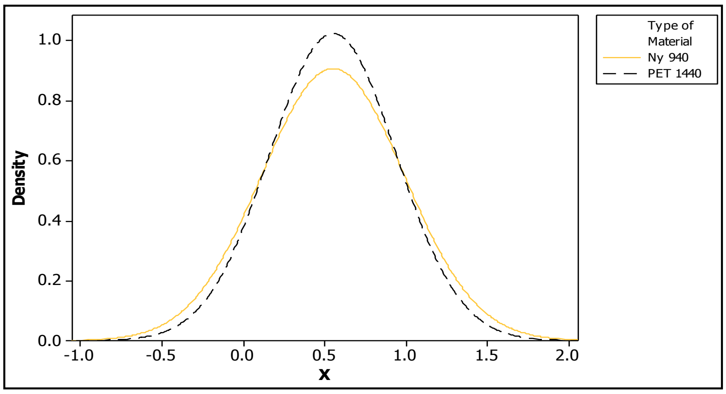

Figure 40- Normalized distribution plot of peel forces for the tested fibers

The peel adhesion results indicate that for both products this test is adequate and this initial analysis does not indicate repeatability and reproducibility problems. For both nylon 940 and PET 1440 a sample size of 1 spool is required to ensure that the sample mean contains the population mean.

With all the test results completed, it is possible to assess which methods comply with the required precision. It is also possible to determine which of the materials influence the most the results, i.e. the number of spools. The number of samples that should be tested for each stage of the manufacturing process and also which test influenced this value the most are expressed in Table 24 and Table 25. Most results indicate that dipped cords require smaller number of samples. For nylon 940, thermal shrinkage is the testing method that requires testing higher number of spools. This method is highly influenced by the type of material, conditions of the laboratory environment and other problems that may exist without being detected

Table 24- Main Results for nylon 940x1x2 for each type of test

	State of the yarn / Cord		
Type of test	**Greige Yarn**	**Greige Cord**	**Dipped Cord**
Linear Density	1	1	1
Load-Elongation	1	3	1
Thermal Shrinkage	8	--	6
Thermal Shrinkage-force	1	--	1
Thickness	13	7	1
Twist Level	1	1	1
Ply Difference	--	+500	--
Peel Adhesion	--	--	1

Most results indicate that dipped cords require testing a smaller number of samples. For nylon 940, thermal shrinkage is the testing method that requires testing larger number of spools. This method is highly influenced by the type of material, conditions of the laboratory environment and other problems that may exist without being detected. As said before, these results indicate that this test method should be studied in detail, comparing the devices results and deviations to other devices, testing different types of fibers and also study the influences of other existing factors on this process. The main results for PET 1440 are in Table 25.

Table 25- Main Results for PET 1440x1x2 for each type of test

	State of the yarn / Cord		
Type of test	**Greige Yarn**	**Greige Cord**	**Dipped Cord**
Linear Density	1	1	1
Load-Elongation	2	3	5
Thermal Shrinkage	6	--	4
Thermal Shrinkage-force	3	--	4
Thickness	10	4	1
Twist Level	1	1	1
Ply Difference	--	+500	--
Peel Adhesion	--	--	1

Thermal-shrinkage and shrinkage-force require a high number of spools for PET 1440. Load-elongation results also display a higher number of spools compared to nylon 940. This is due to inconsistencies and variations on the measurements obtained leading to a higher deviation.

This may be an indicator that this raw material from this specific supplier has consistency issues and should be studied further in order to understand the implications on the final industrial product.

Ply difference and thickness results did not comply with the required precision. These two methods need to be regarded only as qualitative methods or be revised and altered to fit the intended purposes and show results that are applicable in the industrial environment.

It is possible to conclude that tests for linear densities, adhesion and twist level the change of materials did not influence the final results. However for load-elongation, thermal shrinkage and shrinkage-force different fibers and also the state of the fiber (yarn/cord; greige/dipped) result in a different sample size.

Different results can be obtained by changing the confidence level and the margin of error established. However, confidence levels inferior to 90 % and margins of error superior to 10 % of the established mean are not recommended.

4.2 Gage Repeatability and Reproducibility Study

As previously stated, on the second stage of this dissertation the variations between operators and conditions were evaluated using a *Gage R&R study*. This study was performed with two 2 randomly selected spools of nylon 940x1x2 by 5 different operators from the product industrialization laboratory. The tests were performed in a random order according to the procedures and in the same conditions. Breaking force and maximum elongation were the parameters studied on load-elongation curves since on this specific product the previous study of variation showed higher deviations when compared to the other parameters in that test. It was also analyzed the peel adhesion test method. The main results of the deviations and the estimated contribution using variance components (*varcomp model*) obtained from the *Gage R&R* study are in Table 26.

Table 26- Results of the Gage R&R study

	Peel Force		Breaking force		Maximum Elongation	
Source	**S / N**	**% Contribution**	**S / N**	**% Contribution**	**S / %**	**% Contribution**
Total Gage R&R	11	100	1.97	89	0.84	98
Repeatability	7	42	1.78	76	0.67	63
Reproducibility	9	58	0.86	12	0.50	35
Operators	0	0	0.27	2	0.34	16
Operators x Parts	9	58	0.81	11	0.37	19
Part-To-Part	0	0	0.36	11	0.12	2
Total Variation	**11**	**100**	**2.01**	**100**	**0.85**	**100**

From Table 26 it is possible to observe that the total variations were higher than in the previous study. This can easily be explained since the other trials were performed under repeatability conditions. From the analysis of Table 26, it is possible to conclude that the variation for the tested variables is almost entirely explained by variations due to repeatability and reproducibility issues. This shows that the measuring system needs to be upgraded. In a good measuring system most variation is attributed to part-to-part variation. Due to this fact, no conclusions can be drawn the variations between spools.

It is important to observe the p-values resultant from the ANOVA test (Table 27). In all the variables analyzed, the Gage R&R is not capable to identify the effect of parts and operators on the deviation. However, for peel force and maximum elongation the *p-value* of the interaction between parts and operators are significant meaning that there is an effect of the interactions between parts and operators on the deviation obtained.

Table 27- Results of the analysis of variance test

	p-value		
	Peel Force	**Breaking force**	**Maximum Elongation**
Parts	0.88	0.151	0.319
Operators	0.77	0.459	0.259
Parts x Operators	0.005	0.167	0.056

Another result that needs to be analyzed is the number of degrees of freedom available to estimate the repeatability of the gage. This value should vary from 30 to 45 according to the confidence level. In breaking force and maximum elongation there are 40 degrees of freedom regarding repeatability. On peel force there were 20, which may indicate that for further tests the sample size should be higher.

The total variance of testing results is the sum of the material variance, analytical process variance, operator variance and variance of the operators. The previous results, presented in section 4.1, contain only the material variance, analytical process variance and operator variance, while the variance of the present results for load elongation and peel adhesion of nylon 940x1x2 and include the variance of the operators. The variance difference between the two variances gives the contribution for the total variance of the operators –in Table 28

Table 28- Results of variance due to operators

Parameter	S^2_{total}	$S^2_{Materials\ and\ Methods}$	$S^2_{operators}$
Peel force / N^2	125.00	25.00	100.00
Breaking Force / N^2	4.04	2.00	2.04
Max. Elongation / (%)^2	0.72	0.220	0.501

From Table 28 it is possible to conclude that for peel test most of the variance is in fact due to the operators. For Maximum elongation most of the variance obtained is also mostly due to the operators. Breaking force proves to be the parameter where the variance due to operators is smaller.

With this study it also possible to determine if the operators need training by observation of an R chart. An R chart is a control chart of ranges that graphically displays operator consistency. The R charts for the different variables are on Figure 41, Figure 42 and Figure 43. The plotted points are the differences between the largest and smallest measurements for each part.

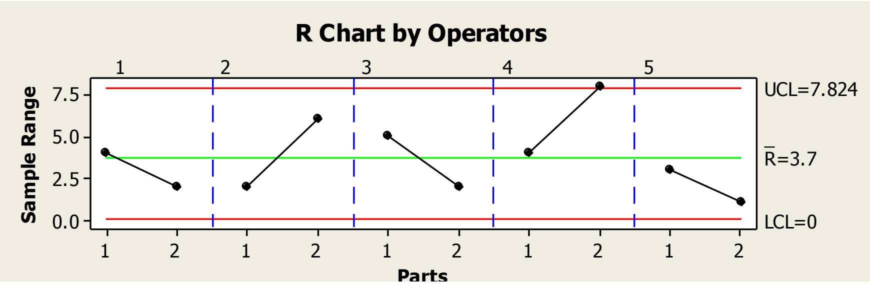

Figure 41 – R Chart by operators for breaking strength

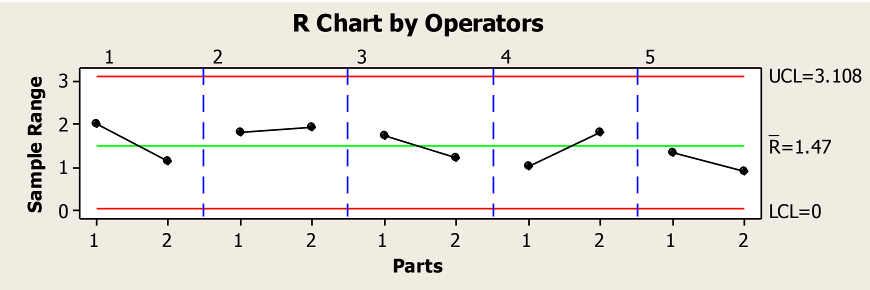

Figure 42- R Chart by operators for maximum elongation

It is possible to observe that regarding load-elongation curves, none of the operators exceeds the upper and lower limit. Therefore, for this test method none of the operators need further training.

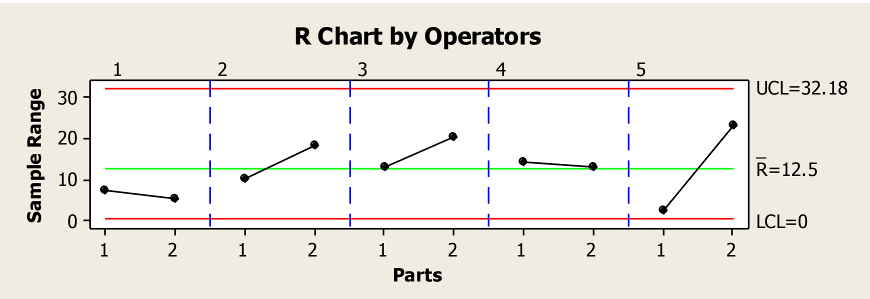

Figure 43- R Chart by operators for peel force

On the peel test the lower control limit is almost reached but still all operators are within the limits. This shows that most operators fall within the control limits. However, the observation off Figure 41, Figure 42 and Figure 43 indicates lack of consistency among operators and between operators and parts.

5 Conclusions

The present dissertation aims at the determination of the number of samples that are required to test with a defined confidence level and margin of error. To achieve this objective 30 spools were tested for two different products and the analysis of normality, distribution and precision was performed.

The methodology developed can be applied to all products; testing 30 spools of each material in all the states of the yarn /cord in order to determine the number of spools required to test with a certain confidence level and margin of error associated should be implemented.

Different test methods had different precision results so the sample size varied according to the testing method, type of fiber and state of the yarn/ cord. Peel adhesion, linear density and load-elongation tests methods have proven to comply with the required precision. Thermal shrinkage and shrinkage-force indicate high sensitivity to the type of fiber tested demanding a larger sample size. A comparison between equipment, calibration procedures and the study of influencing factors should be considered.

Ply difference and thickness showed very high deviations when compared to the samples mean, demanding a very large number of samples (larger than 500 samples for ply difference for a confidence level of 95 % and a margin of error of 5 % of the sample average) not compatible with the industry requirements. These test methods must be considered as qualitative and not quantitative.

Regarding the *Gage R&R*, the obtained results lead to the conclusions that the variance can be almost totally explained by repeatability and repeatability problems. Due to this fact, variations between spools were not possible to determine. This indicates that the methods should be changed. It was also possible to conclude that for all the parameters analyzed the variation due to operators is very high representing more than 50 % of the total variance.

6 Project Assessment

6.1 Accomplished Objectives

The assessment of the number of spools (sample size) required to test was the initial focus of this project. It was unknown the reality behind or the mathematical implications and statistical concepts that would need to be applied. The results were obtained successfully for the two products tested and for all the test methods it was determined that, regarding the products analysed, the sample mean follows approximately the normal distribution. This work also permitted a better characterization of the product regarding expected variances in relation to the test methods, allowing to conclude which methods are not fit to the intended purposes.

6.2 Future Work

In the future it is necessary to establish regular calibration procedures and processes in the Process Industrialization Laboratory. Furthermore, quality control tools should be applied. A detailed study to determine which factors influences variance such as operators, environment, products and processes should be carried out. In addition, the determination of the most influential factors on the applied test methods would be interesting and may indicate which external factor or internal properties of the fiber most affect the results. In addition, the creation of a data base including fibers proprieties and statistical data allows tracking the variations and possibly identifying tendencies in products and/or manufacturers. To evaluate the results within the Continental Group interlaboratory comparison studies would be valuable and contribute to uniformity of the laboratories and may help the certifications the Laboratory.

6.3 Final Assessment

Professionally this was the first of many challenges to come. This project in particular required a lot of patience and also method due to the sensitivity of the methods and also to avoid influencing results. The most difficult part of developing this project was to combine textile reinforcements and statistical treatment and knowledge. This made this type of work really stimulating. Personally it was a way of developing technical and adaptation skills.

7 References

1. S.Moodley, D.A., *An analytical study of vehicle defects and their contribution to road accidents*, in *Department of Civil Engineering and Surveying* 2008, Durban University of Technology: Pretoria.
2. Wennekes, W.B., *Adhesion of RFL-treated cords to rubber*, in *Dutch Polymer Institute*2008, University of Twente: Netherlands. p. 180.
3. Continental Corporation. *Continental Plans to Further Expand Workforce*. 2014 [cited 2014 17 February];Available from: http://www.continental-corporation.com/www/pressportal_us_en/themes/press_releases/1_topics/work_life/pr_2014_03_13_employee_forecast_en.html.
4. Continental Corporation *Tyre Basics Passenger Cars*. 2008 [cited 2014 March 6].
5. Rodger, B., *Rubber Compounding Chemistry and Applications*. 2004, Akron, Ohio: The Goodyear Tire and Rubber Company.
6. Continental-AG, *Corporate Presentation*. 2009.
7. Continental-AG. *Continental Plans to Further Expand Workforce*. 2014 [cited 2014 22 April]; Available from: http://www.continental-corporation.com/www/pressportal_us_en/themes/press_releases/1_topics/work_life/pr_2014_03_13_employee_forecast_en.html.
8. Continental-AG. *The makings of an international corporation*. 2014 [cited 2014 22 April].
9. Burrowes, G. and B. Rodgers, *Reinforcing Materials in Rubber Products*. 2010, Nebraska, United States of America: The Goodyear Tire and Rubber Company.
10. Wahl, G., *Basics of Textile Reinforcement Materials for Tyres*. 2006: Continental.
11. Pinto, D., *Hybrid Technology: A simulation model to predict optimized textile reinforcements properties*, in *Chemical Engineering Department* 2013, Faculty of Engineering of the University of Porto.
12. Gent, A.N. and J.D. Walker, *The Pneumatic Tire*. 2006, United States of America: U.S. Department of Transportation.
13. Kumar, R.S., *Textile for Industrial Application*. 2014, Kumaranguru India: Department of Textile Technology.
14. Yilmaz, B. and V. Deniz, *Effects of Linear Density and Twist Level on the Mechanical Properties of Nylon 6.6 Tyre Cords*, 2009, Department of Chemical Engineering: Kocaeli Turkey.
15. Gurbuz, R., *Tension Test*, 2006, Middle East Technical University: Ankara Turkey.
16. Urudzhev, R.S., *The Thermal Shrinkage of Textile Fibers*. 2009.
17. Voloshin, A. and B. Emri, *Effect of Heating on Fiber Shrinkage* 2008, Department of Mechanical Engineering and Mechanics: United States of America.
18. Yilmaz, B., V. Deniz, and A. Aytac, *Effect of Twist Level on Tyre Cord Performance*. Fibers and Polymers, 2009. **10**.
19. Hockenberger, A.S. and S. Koral, *Effect of twist level on the performance of tire cord yarns*. Indian Journal of Fiber & Textile 2004. **29**.
20. Direito, F., *Know how and key process parameters for water based latex dip formulations to get robust reinforcement-to-rubber adhesion in passanger car tyres*,

in *Chemical Engineering Department* 2011, Faculty of Engineering of University of Porto.

21. ASTM International, *D 4776-09: Standard Test Method for Adhesion of Tire Cords and Other reinforcing Cords To Rubber Compounds by H-test Procedure*. 2009.
22. Vale, R., *Quality Testing Procedures Implemented at C-ITA*, 2007, Indústria Têxtil do Ave: Lousado.
23. International Organization for Standardization, *ISO 5725: Precision of test methods - Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests*. 2012.
24. In*ternational Organization for Standardization*, *ISO 17025 : General requirements for the competence of testing and calibration laboratories*. 2010.
25. International Organization for Standardization., *ISO 21748 : Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation*. 2010.
26. Miller, J.N. and J.C. Miller, *Statistics and Cheometrics for Analytical Chemistry*. Sixth ed. 2010: Pearson Education Limited.
27. Montogomery, D.C. and G.C. Runger, *Applied Statistics and Probability for Engineers* Third ed. 2003: John Wiley & Sons, Inc.
28. M.Ross, S., *Introduction to Probability and Statistics for Engineers and Scientists*. Third ed. 2004, USA: Elsevier Academic Press.
29. *Engineering Statistics Handbook*. 2013 [cited 2014 April 25]; Available from: http://www.itl.nist.gov/div898/handbook/index.htm.
30. Pandiripalli, B., *Repeatability and Reproducibility Studies : A Comparison of Techniques*, in *Department of Industrial and Manufacturing Engineering* 2010, Faculty of the Graduate School of Whicita State University: Kansas USA.
31. Stephenson, W.R., *Gage Repeatability and Reproducibility*, in *Department of Statistics* 2008, Iowa State University: USA.
32. ASTM International, *D1776: Standard Practice for Conditioning and Testing Textiles*. 2008.
33. ASTM International, *ASTM D885: Standard Test Methods for Tire Cords, Tire Cord Fabrics, and Industrial Filament Yarns Made from Manufactured Organic-Base Fibers*. 2014.
34. ASTM International, *D 5591:Standard Test Method for Thermal Shrinkage Force of Yarn and Cord With a Thermal Shrinkage Force Tester*. 2011.
35. International Organization for Standardization, *ISO 2061: Textiles Determination of twist in yarns - Direct counting method*. 2013.
36. ASTM International, *ASTM D4776: Standard Test Method for Adhesion of Tire Cords and Other Reinforcing Cords to Rubber Compounds by H-Test Procedure*. 2012.

8 Annex

The present annexes include standard score values according to confidence level, a summarized table of results of all parameters tested in each test method applied for all the states of the yarn / cord for both materials tested. Also, the main results for Gage R&R before the statistical treatment applied.

Annex I- Z values according to the confidence level

Table 29- z-values according to the confidence level

Confidence Level / %	Significance (α)	$\alpha/2$	*z-value*
50	0,5	0,25	0,67
60	0,4	0,2	0,841
70	0,3	0,15	1,036
80	0,2	0,1	1,282
85	0,15	0,075	1,44
90	0,1	0,05	1,645
95	0,05	0,025	1,96
98	0,02	0,01	2,33
99	0,01	0,005	2,58

Annex II- Results for nylon 940 and PET 1440 cords

Table 30- Results for nylon 940 greige yarns

Test Method/ Properties	*Parameter*	$\bar{X}$	*S*	*n / nº spools*
Thickness	Thickness	0.134	0.012	13
Load-Elongation	Fase 2 % / N	11.85	0.26	1
	Fase 4 % / N	18.44	0.34	1
	Fase 6 % / N	26.98	0.61	1
	Fase 8 % / N	39.66	0.93	1
	Fase 12 % / N	78.32	1.77	1
	Breaking Strength /N	144.49	2.28	1
	Elongation @20N / %	4.43	0.10	1
	Elongation @25N / %	5.61	0.11	1
	Elongation @45N / %	8.68	0.13	1
	Elongation @ Max / %	16.82	0.44	1
Thermal Shrinkage	Effective Thermal Shrinkage / %	4.97	0.34	8
	Residual Thermal Shrinkage / %	3.19	0.28	12
T. Shrinkage-force	Effective T. Shrinkage-force / %	288	5.9	1
	Shrinkage-force Residual / %	10.46	4.52	287
Linear Density	Decitex / g×10 000 m^{-1}	914.23	15.3	1

Table 31- Results for nylon 940 greige cords

Test Method/ Properties	***Parameter***	$\overline{X}$	***S***	***n / nº spools***
Thickness	Thickness	0.43	0.027	7
Load-Elongation	Fase 2 % / N	11.85	0.027	1
	Fase 4 % / N	18.44	0.26	1
	Fase 6 % / N	26.98	0.34	1
	Fase 8 % / N	39.66	0.61	1
	Fase 12 % / N	78.32	0.93	1
	Breaking Strength /N	144.49	1.77	1
	Elongation @20N / %	4.43	2.28	1
	Elongation @25N / %	5.61	0.10	1
	Elongation @45N / %	8.68	0.11	1
	Elongation @ Máx / %	20.84	0.13	3
Twist	Cord twist /tpm	343	6	1
	Yarn twist /tpm	346	6	1
Linear Density	Decitex / g×10 000 m^{-1}	1944.33	5.59	1
Ply Difference	Ply Difference / mm	4	2	+500

Table 32- Results for nylon 940 dipped cords

Test Method/ Properties	***Parameter***	$\overline{X}$	***S***	***n / nº spools***
Thickness	Thickness	0.56	0.015	1
Load-Elongation	Fase 2 % / N	12.77	0.17	1
	Fase 4 % / N	20.68	0.28	1
	Fase 6 % / N	32.59	0.48	1
	Fase 8 % / N	49.86	0.76	1
	Fase 12 % / N	97.27	1.26	1
	Breaking Strength /N	148.06	1.41	1
	Elongation @20N / %	3.90	0.06	1
	Elongation @25N / %	4.83	0.06	1
	Elongation @45N / %	7.51	0.07	1
	Elongation @ Max / %	19.78	0.91	1
Thermal Shrinkage	Effective Thermal Shrinkage / %	4.7	0.28	6
	Residual Thermal Shrinkage / %	2.50	0.18	8
T. Shrinkage-force	Effective T. Shrinkage-force / %	529.24	1.38	1
	Shrinkage-force Residual / %	8.20	5.4	670
Peel Adhesion test	Average Distance /mm	82.42	2.12	1
	Peel Force /N	197	5	1
	Appearance	5	0	1
Twist	Cord twist /tpm	340	5	1
	Yarn twist /tpm	339	4	1
Linear Density	Weight per length / g×100 m^{-1}	20.04	0.27	1

Table 33- Results for PET 1440 greige yarns

Test Method/ Properties	***Parameter***	$\bar{X}$	***S***	***n / nº spools***
Thickness	Thickness	0.134	0.012	13
Load-Elongation	Fase 2 % / N	11.85	0.26	1
	Fase 4 % / N	18.44	0.34	1
	Fase 6 % / N	26.98	0.61	1
	Fase 8 % / N	39.66	0.93	1
	Fase 12 % / N	78.32	1.77	1
	Breaking Strength /N	144.49	2.28	1
	Elongation @20N / %	4.43	0.10	1
	Elongation @25N / %	5.61	0.11	1
	Elongation @45N / %	8.68	0.13	1
	Elongation @ Máx / %	16.82	0.44	1
Thermal Shrinkage	Effective Thermal Shrinkage / %	4.97	0.34	8
	Residual Thermal Shrinkage / %	3.19	0.28	12
T. Shrinkage-force	Effective T. Shrinkage-force / %	288	5.9	1
	Shrinkage-force Residual / %	10.46	4.52	287
Linear Density	Decitex / g×10 000 m^{-1}	914.23	15.3	1

Table 34-Results for PET 1440 greige cords

Test Method/ Properties	***Parameter***	$\bar{X}$	***S***	***n / nº spools***
Thickness	Thickness	0.55	0.025	4
Load-Elongation	Fase 2 % / N	23.73	0.443	1
	Fase 4 % / N	42.63	0.592	1
	Fase 6 % / N	63.21	0.862	1
	Fase 8 % / N	87.75	1.143	1
	Fase 12 % / N	143.80	1.460	1
	Breaking Strength /N	178.18	2.145	1
	Elongation @20N / %	1.67	0.047	2
	Elongation @25N / %	2.13	0.044	1
	Elongation @45N / %	4.25	0.065	1
	Elongation @ Max / %	16.25	0.63	3
Twist	Cord twist /tpm	367	5	1
	Yarn twist /tpm	377	5	1
Linear Density	Decitex / g×10 000 m^{-1}	3141.00	22.96	1
Ply Difference	Ply Difference / mm	3	2	

Table 35- Results for PET 1440 dipped cords

Test Method/ Properties	***Parameter***	$\bar{X}$	***S***	***n / nº spools***
Thickness	Thickness	0.631	0.011	1
Load-Elongation	Fase 2 % / N	39.16	0.59	1
	Fase 4 % / N	71.04	0.80	1
	Fase 6 % / N	103.11	1.10	1
	Fase 8 % / N	135.14	1.35	1
	Fase 12 % / N	136.75	0.61	1
	Breaking Strength /N	178.41	3.01	1
	Elongation @20N / %	0.92	0.06	5
	Elongation @25N / %	1.17	0.03	1
	Elongation @45N / %	2.36	0.04	1
	Elongation @ Máx / %	11.92	0.48	3
Thermal Shrinkage	Effective Thermal Shrinkage / %	4.0	0.1	2
	Residual Thermal Shrinkage / %	3.85	0.20	4
T. Shrinkage-force	Effective T. Shrinkage-force / %	688.11	21.53	2
	Shrinkage-force Residual / %	342.54	17.73	4
Peel Adhesion test	Average Distance /mm	80.10	0.72	1
	Peel Force /N	178	4	1
	Appearance	5	0.5	1
Twist	Cord twist /tpm	359	2	1
	Yarn twist /tpm	369	2	1
Linear Density	Weight per length / g×100 m^{-1}	31.84	0.32	1

Annex III- Data for the Gage R&R study

Table 36- Peel force data for Gage R&R study

Run Order	Parts	Operators	Peel Force / N
1	1	1	168
2	1	2	172
3	1	3	168
4	1	4	174
5	1	5	191
6	2	1	169
7	2	2	170
8	2	3	165
9	2	4	176
10	2	5	177
11	1	1	161
12	1	2	166
13	1	3	173
14	1	4	181
15	1	5	193
16	2	1	173
17	2	2	169
18	2	3	185
19	2	4	184
20	2	5	170
21	1	1	167
22	1	2	162
23	1	3	181
24	1	4	167
25	1	5	192
26	2	1	168
27	2	2	187
28	2	3	175
29	2	4	171
30	2	5	154

Table 37- Load-Elongation data for Gage R&R study

Parts	Operators	Breaking Strength /N	Elongation Max / %	Parts	Operators	Breaking Strength /N	Elongation Max / %
1	1	151	21.2	2	1	151	21.3
1	2	149	20.1	2	2	146	19.2
1	3	150	21.2	2	3	149	20.5
1	4	148	20.3	2	4	147	20.3
1	5	149	20.8	2	5	149	20.5
2	1	149	20.5	1	1	149	20.7
2	2	148	20	1	2	149	19.9
2	3	148	19.8	1	3	151	19.5
2	4	143	18.9	1	4	152	21.2
2	5	150	21	1	5	152	22.1
1	1	149	20.5	2	1	151	21.6
1	2	148	19.4	2	2	149	19.7
1	3	150	20	2	3	149	19.5
1	4	150	20.6	2	4	151	20.7
1	5	151	21.3	2	5	149	20.1
2	1	150	20.8	1	1	151	21.5
2	2	152	21.1	1	2	148	18.6
2	3	147	19.3	1	3	146	20.7
2	4	148	19.8	1	4	152	20.8
2	5	150	20.9	1	5	152	21.7
1	1	149	19.5	2	1	151	21.2
1	2	150	20.4	2	2	149	19.6
1	3	150	20.9	2	3	149	20.1
1	4	151	21.3	2	4	148	19.2
1	5	150	20.8	2	5	149	20.3